ABSTRACT

Title of Dissertation:	REMOVAL OF STORMWATER DISSOLVED ORGANIC NITROGEN MODEL COMPOUNDS THROUGH ADSORPTION AND BIOTRANSFORMATION
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Bioretention systems are stormwater control measures designed to reduce nitrogen and phosphorus transferred by stormwater to water resources. They are, however, not effectively designed to remove dissolved organic nitrogen (DON). This study concentrated on improvement of bioretention design to remove stormwater DON. Batch adsorption of eight organic nitrogenous compounds onto several adsorbents showed that coal activated carbon (AC) could be a reliable adsorbent for removal of organic nitrogenous compounds such as pyrrole and N-acetyl-D-glucosamine (NAG). The adsorption capacity of pyrrole and NAG on coal AC were 0.4 mg N/g (at equilibrium concentration, C_e = 0.02 mg N/L) and 0.71 mg N/g (at C_e = 1 mg N/L),

respectively. These eight nitrogenous compounds were also tested for continuous column adsorption on a media mixture of coal AC + quartz sand, and only pyrrole showed an appreciable adsorption performance; the breakthrough and exhaustion depths for pyrrole were 88 and 499 m, respectively, at the fixed superficial velocity of 61 cm/h and influent DON concentration of 1 mg N/L. Pyrrole adsorption was also minimally affected by superficial velocity (DON removal efficiency stayed > 91% for all tested superficial velocities, 7 to 489 cm/h).

Because the adsorption process was successful for removal of only one (pyrrole) out of eight examined compounds, biological treatment was also investigated for removal of organic nitrogenous compounds. Biotransformation alongside adsorption demonstrated benefits such as ammonification of bio-recalcitrant organic nitrogen compounds, e.g., pyrrole, and bioregeneration of the adsorbent (coal AC). According to the results, ammonifiction might be considered as a possible reliable mechanism for stormwater DON removal at low temperatures > 4°C. Under intermittent wetting/draining conditions, the effluent DON was less than 0.1 mg N/L after the applied depth of 48 m, indicating that DON was successfully removed through simultaneous adsorption/ammonification, although generated ammonium in the effluent must be properly addressed. Overall, based on the results from the current study, some DON types were strongly adsorbed by adsorbents, e.g., adsorption of pyrrole on coal AC, some were more bioavailable, e.g., ammonification of leucine, and some were barely adsorbable and bioavailable, e.g., Aldrich humic acid on coal AC. Accordingly, both adsorption and biotransformation should be considered to enhance stormwater DON removal as much as possible.

REMOVAL OF STORMWATER DISSOLVED ORGANIC NITROGEN MODEL COMPOUNDS THROUGH ADSORPTION AND BIOTRANSFORMATION

by

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Dissertation submitted to the Faculty of the Graduate School of the
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Dedication

To my mom and dad for their endless support and unstinting devotion.

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complex situation. She kindly addressed all my academic issues and always supported me with positive energy. I really appreciate her for everything she has done for me.

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List of Abbreviations

AC	Activated Carbon
AHA	Aldrich Humic Acid
DI	Deionized
DON	Dissolved Organic Nitrogen
LID	Low Impact Development
NAG	N-Acetyl-D-Glucosamine
NH_4^+-N	Ammonium Nitrogen
NO_3^--N	Nitrate Nitrogen
NO_2^--N	Nitrite Nitrogen
PON	Particulate Organic Nitrogen
SCMs	Stormwater Control Measures
TN	Total Nitrogen
TDN	Total Dissolved Nitrogen
WTR	Water Treatment Residual

Chapter 1: Introduction

Urbanization severely impacts both quantity and quality of stormwater. Urban impervious surfaces reduce infiltration and increase surface runoff, leading to increase in transport and delivery of pollutants (e.g., sediment, nutrients, pesticides, toxic metals, organic compounds, oil and grease) to waterbodies (U.S. EPA, 1996, 1999). The nutrients, especially nitrogen and phosphorus, transferred by stormwater from land surfaces to water bodies, can potentially accelerate eutrophication (U.S. EPA, 1996, 1999; Stumm and Morgan, 2013).

Nitrogen wash-off from urban areas is a source-limiting process, meaning that stormwater can remove most nitrogen from surfaces (Miguntanna et al., 2013). Generally, nitrogen compounds in stormwater are available in two forms: organic and inorganic (Duncan, 1999). Examples of organic nitrogen are proteins, peptides, amino acids, amino sugars, heterocyclic nitrogen, etc., and inorganic nitrogen mainly includes ammonium, nitrate, and nitrite (Lide, 2004). Inorganic nitrogen is available in dissolved form, while organic nitrogen can be found in both forms of dissolved and particulate. Although the concentrations of nitrogen species are highly variable, organic nitrogen appears to be the major form of nitrogen in urban stormwater, making up more than half of total nitrogen (TN) as seen in Figure 1-1. Compared to particulate organic nitrogen (PON), dissolved organic nitrogen (DON) constitutes a smaller fraction of TN. DON, along with nitrate, forms the major part of total dissolved nitrogen in urban stormwater. According to past studies (Li and Davis, 2014; Taylor et al., 2005), DON forms 15-28% of TN while nitrate makes up 19-35% (Figure 1-1). Miguntanna et al.

(2013) also indicated that the major form of nitrogen in stormwater runoff is dissolved and organic, and can be easily washed off by even a low intensity rainfall. Therefore, organic nitrogen removal is an important consideration for targeting nitrogen removal treatment design.

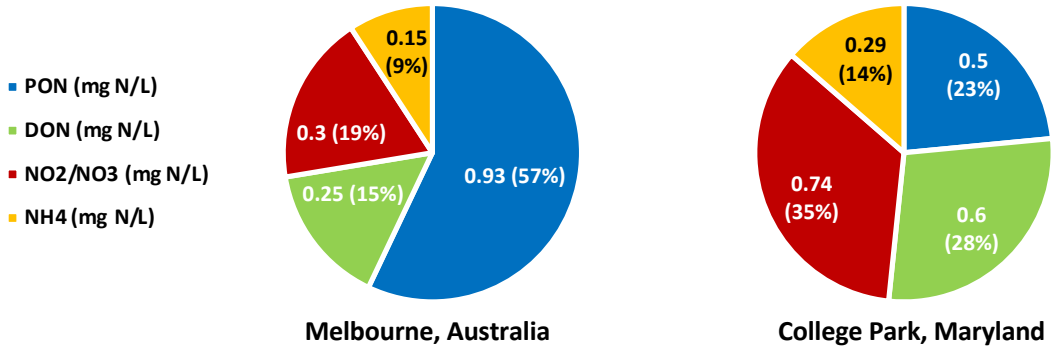

Figure 1-1. Available forms of nitrogen and their concentrations in urban stormwater runoff (Taylor et al., 2005; Li and Davis, 2014)

Stormwater Control Measures (SCMs) are infrastructures have been employed to reduce runoff and remove pollutants from stormwater. They also provide flood control, reduce downstream erosion, and promote groundwater recharge (U.S. EPA, 1993, 1999; Davis and McCuen, 2005; Davis, 2007; Bratieres et al., 2008; Davis et al., 2009; Roy-Poirier et al., 2010; Liu et al., 2016).

A type of SCM is bioretention which employs a set of abiotic (e.g., adsorption and filtration) and biotic (e.g., biological degradation and plant uptake) mechanisms to remove pollutants from stormwater (LeFevre et al., 2015). A schematic diagram of bioretention is presented in Figure 1-1. While bioretention systems have been effective in removal of PON from stormwater, removal of dissolved nitrogen has been challenging because dissolved nitrogen, especially nitrate and nitrite, have high

solubility and cannot be appreciably adsorbed by bioretention media (Li and Davis, 2014; LeFevre et al., 2015).

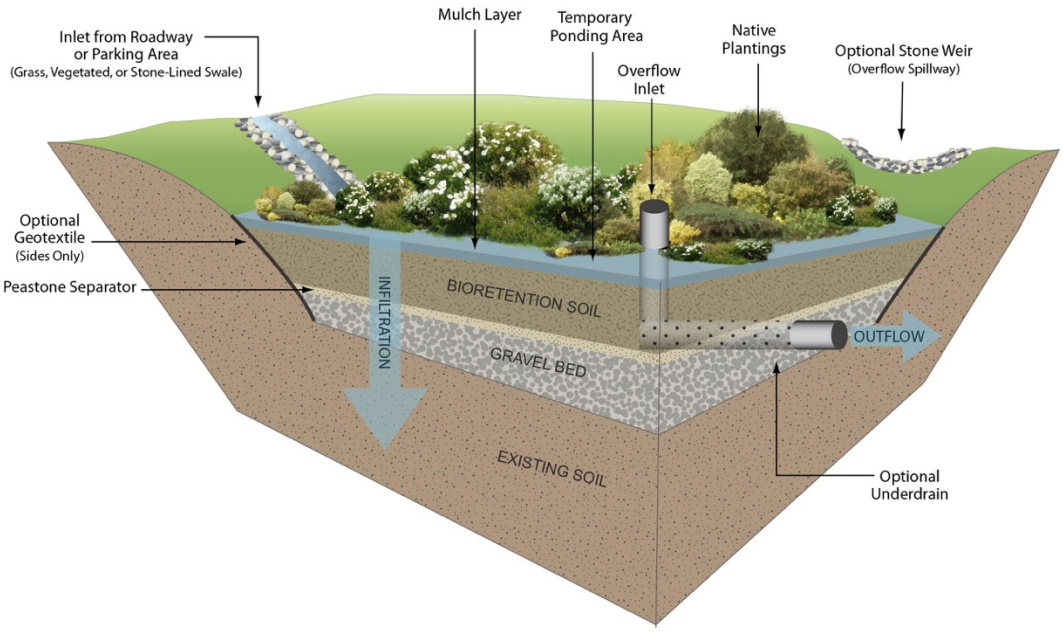

Figure 1-2. A schematic diagram of bioretention (courtesy of GeoSyntec Consultants)

Unlike nitrate and nitrite, ammonium can be limitedly adsorbed by some materials, including clays, zeolites and silicates through cation-exchange processes (Rožić et al., 2000; Hedström, 2001; Khorsha and Davis, 2017b, 2017a). Similar to the soil environment, a series of biochemical reactions, mediated by microbes, could determine the fate of dissolved nitrogen in bioretention (Robertson and Groffman, 2015). These biochemical reactions are (Figure 1-3): (1) ammonification: transformation of dissolved organic nitrogen (DON) to ammonium, which occurs under both aerobic and anaerobic conditions; (2) nitrification: transformation of ammonium to nitrite and then to nitrate under aerobic conditions; (3) denitrification: transformation of nitrate to nitrogen gas under anoxic conditions (Rittmann and McCarty, 2001). These biochemical reactions have been examined and employed to remove dissolved

nitrogen, mainly inorganic nitrogen. Creation of a denitrification zone, referred to an internal water storage (IWS), in bioretention has been shown to enhance removal of stormwater nitrate/nitrite. The IWS is designed to stay saturated between storm events and develop anoxic conditions promoting denitrification (Kim et al., 2003; Hsieh et al., 2007; Ergas et al., 2010; Peterson et al., 2015; Igielski et al., 2019). Ammonium has also been shown to be removed through adsorption on sandy coarse/fine soil layer during stormwater dosing followed by nitrification during subsequent dry periods (Cho et al., 2009). However, much less is known about the composition of DON in urban stormwater and its removal and fate in bioretention. Moreover, it has been found that bioretention facilities may become net nitrogen exporters by releasing DON, likely due to dissolution and conversion of influent PON and vegetation residuals to DON (Li and Davis, 2014). Overall, incorporating a mechanism for DON removal from stormwater runoff can be highly beneficial to increasing the removal efficiency of stormwater total nitrogen.

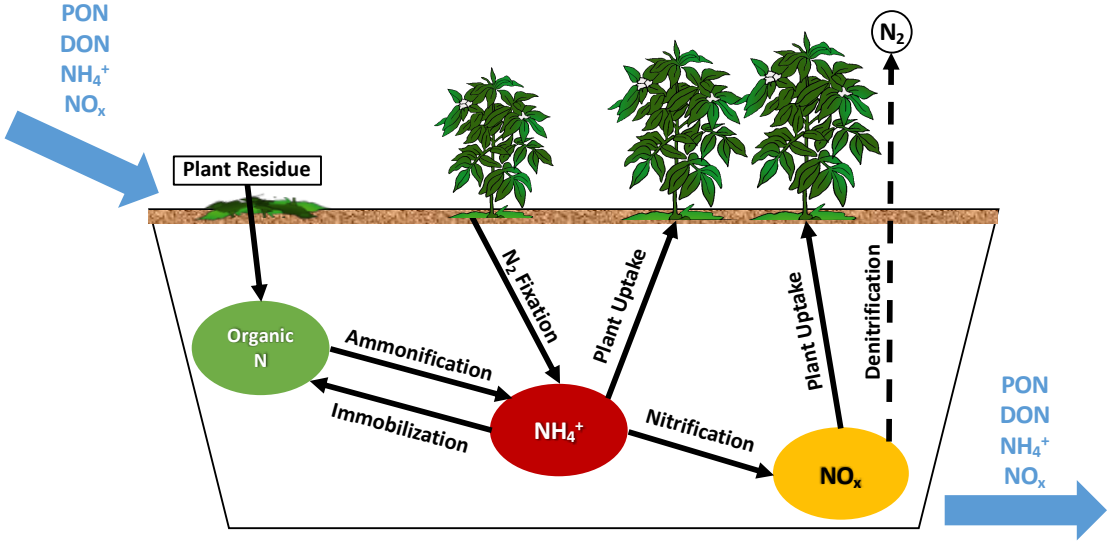

Figure 1-3. Possible nitrogen cycle in bioretention

Regarding DON adsorption, clays (e.g., kaolinite and montmorillonite), silica, and zeolites adsorb and store some amino acid types (arginine, leucine, isoleucine, methionine, phenylalanine) through cation-exchange or hydrophobic interactions (Basiuk and Gromovoy, 1996; Hedges and Hare, 1987; Krohn and Tsapatsis, 2005; Nannipieri and Smalla, 2006). Other studies have shown that humic acid can be adsorbed by zeolite, kaolinite, bentonite, chitosan, activated carbon, and xonotlite (Katsumata et al., 2003; Zhang and Bai, 2003; Salman et al., 2007; Maghsoodloo et al., 2011; Moussavi et al., 2011; Shaker et al., 2012). By retaining stormwater DON through adsorption, bioretention may provide enough time for plants to directly take up DON; a study by Näsholm et al. (2009) confirms the ability of plants to directly acquire amino acids from soil. 45-70% of rainwater dissolved organic nitrogen was found to be biologically available (Chen et al., 2011). Karanfil (2006) found that biofilters removed non-adsorbable organic matter from drinking water and the efficiency of adsorption improved with increased levels of biological activity, providing evidence of bioregeneration. Simultaneous adsorption and biotransformation may positively or negatively affect the biodegradation process of organic compounds. Adsorbed compounds may be less bioavailable because they are less likely to be present in aqueous phase (Gordon and Millero, 1985; Ogram et al., 1985; Robinson et al., 1990; Smith et al., 1992; Knaebel et al., 1996; Nam et al., 1998;). On the other hand, it has been reported that attached microbes may benefit from slow biodegradation of adsorbed compounds because of longer detention time (Griffith and Fletcher, 1991; Marchesi et al., 1997; Carlson and Silverstein, 1998). Overall, adsorption followed by

biological treatment are suggested to be examined for stormwater DON removal in bioretention systems.

Research Goal

The overall goal of this research was to find appropriate materials and evaluate their performance in adsorption of stormwater DON along with formation of biofilms that can lead to mineralization of stormwater DON to ammonium.

Research Objectives

This research was carried out in three phases: (1) batch adsorption studies, (2) column adsorption studies, and (3) biotransformation studies. The batch adsorption studies were the first steps to evaluate different adsorbents, determine their capability in stormwater DON removal, and select the materials with the best adsorption performance for advancement to column study. The column study was to evaluate the performance of the adsorbent(s) in stormwater DON removal under more realistic conditions (continuous flowrate) and determine the potential of the adsorbent(s) in retaining stormwater DON in long-term performance. The final phase, biotransformation study, concentrated on the possibility for removal of stormwater DON (specifically poorly-adsorbable DON) through biochemical processes (specifically ammonification), and possible bioregeneration of the adsorbents. Specific research objectives were pursued to achieve the project goal. These were to:

- evaluate batch adsorption of selected organic nitrogenous compounds on selected adsorbents (selected organic nitrogenous compounds are employed to represent and reflect the properties of expected common stormwater organic nitrogenous

compounds), to investigate if adsorption can be employed for stormwater DON removal in bioretention.

- determine batch adsorption factors, e.g., adsorption capacity and adsorption kinetics, to select long-lasting material(s) which are able to effectively adsorb stormwater DON such that these materials can be used as a component of bioretention media.
- evaluate column adsorption of the selected organic nitrogenous compounds on the adsorbent(s) that showed the best performance in batch adsorption study, to investigate the performance of the adsorbent(s) in more realistic conditions.
- determine breakthrough and exhaustion times in long-term column adsorption experiments, to estimate bioretention media lifetime used for stormwater DON removal.
- examine the effect of water flowrate (column adsorption kinetics) and media bed height on column adsorption capacity, to find a practical water retention time and media bed height to improve bioretention design for stormwater DON removal.
- evaluate biotransformation (specifically ammonification) of the selected organic nitrogenous compounds, to investigate if biochemical processes are reliable mechanisms for stormwater DON removal.
- examine the ammonification of organic nitrogenous compounds with different levels of bioavailability and adsorbability on bioretention media to investigate ammonification of stormwater bio-recalcitrant DON, bioregeneration of

bioretention media, and positive/negative effects of adsorption on stormwater DON ammonification.

- assess the effect of bed media with different properties (e.g., pore volume, average pore size, specific surface area, and porosity) on ammonification process to see if less expensive material can be used as bioretention media enhancing ammonification of stormwater DON.
- examine the effect of contact time between organic nitrogenous compounds and biofilm on ammonification process by changing water flowrate and bed media height, and find practical water flowrate and bed media height to improve bioretention design for ammonification of stormwater DON.
- test the extent of the effect of a cold weather condition (4°C) on ammonification process, to examine stormwater DON removal through biotransformation in bioretention during winter season;
- evaluate the ammonification process under a wetting/draining regime, which is a more realistic condition, to test the hypothesis that intermittent wetting/draining conditions would enhance ammonification and bioregeneration of bioretention media by providing enough time for microbial activity between storm events.

Chapter 2: Batch Adsorption of Compounds that Mimic Urban Stormwater Dissolved Organic Nitrogen

Abstract

Stormwater runoff carrying nitrogen can accelerate eutrophication. Bioretention facilities are among low impact development systems which are commonly used to manage urban stormwater quality and quantity. They, however, are not designed to remove dissolved organic nitrogen (DON) and may become a net DON exporter. Adsorption of eight organic nitrogenous compounds onto several adsorbents was examined. Batch adsorption study revealed that coal activated carbon (AC) exhibited the best performance in adsorption of the selected organic nitrogenous compounds. The highest adsorption capacity of coal AC was 0.4 mg N/g for pyrrole at an equilibrium concentration of 0.02 mg N/L, while adsorption was not detectable for urea at the same equilibrium concentration. The fastest compound to reach equilibrium adsorption capacity onto the coal AC was pyrrole (1 hour). The adsorption capacity of the coal AC for pyrrole and N-acetyl-D-glucosamine and 1-hour contact time is recommended for designing bioretention systems targeting organic nitrogenous compounds.

Keywords: Stormwater, Bioretention, Rain garden, Nitrogen, Runoff, Eutrophication, Nutrients

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Introduction

Stormwater runoff carrying nutrients such as nitrogen and phosphorus from land surfaces to water bodies can potentially accelerate eutrophication (U.S. EPA, 1996). According to two separate studies conducted in the United States and Australia (Table 2-1), the mean concentration of total nitrogen (*TN*) in urban stormwater runoff is 1.62 and 2.13 mg N/L, respectively (Li and Davis, 2014; Taylor et al., 2005). Although the concentrations of nitrogen species are highly variable, total organic nitrogen appears to be the major form of nitrogen in urban stormwater runoff, making up more than half of total nitrogen. Compared to particulate organic nitrogen (*PON*), dissolved organic nitrogen (*DON*) constitutes a smaller fraction of TN. The DON fraction is close to that of nitrate; 19% nitrate vis-à-vis 15% DON in the Maryland study and 35% nitrate/28% DON in the Australia study. Therefore, DON removal from stormwater runoff is as important as nitrate removal and can significantly contribute to TN removal.

Table 2-1. Available forms of nitrogen and their concentrations in urban stormwater runoff according to recent studies

Source of runoff	**Mean concentration (mg N/L)**					**Reference**
	TN	**PON**	**DON**	**NO_x^-**	**NH_4^+**	
Urban land use (College Park, MD, USA)	1.62	0.93	0.25	0.30	0.15	Li and Davis (2014)
Urban land use (Melbourne, Australia)	2.13 ± 0.79	0.50 ± 1.11	0.60 ± 0.93	0.74 ± 0.76	0.29 ± 1.73	Taylor et al. (2005)

Bioretention facilities are among low impact development (LID) systems which are employed to manage stormwater quantity and quality. They employ a set of abiotic (e.g., adsorption and filtration) and biotic (e.g., biological degradation and plant uptake) mechanisms to remove particulate and dissolved nutrients, organic compounds, and

toxic metals (LeFevre et al., 2015). While bioretention facilities are effective in PON removal, dissolved nitrogen removal from stormwater runoff remains a challenge (Li and Davis, 2014; LeFevre et al., 2015).

Ammonium can be limitedly adsorbed by some materials, including clays and zeolites, through cation-exchange mechanisms (Rožić et al., 2000; Hedström, 2001). Highly soluble nitrate/nitrite are minimally adsorbed by any bioretention media. In this regard, recent studies have been concentrated on application of biotic processes to remove nitrate/nitrite from stormwater runoff. An anoxic water-saturated zone containing organic carbon should promote denitrification and consequently nitrate removal in bioretention facilities (Kim et al., 2003; Hsieh et al., 2007; Ergas et al., 2010; Peterson et al., 2015). Peterson et al. (2015) reported up to 82% nitrate removal throughout the anoxic water-saturated zone. Moreover, vegetation may increase nitrate removal in bioretention facilities (Henderson et al., 2007; Lucas and Greenway, 2008). For instance, Henderson et al. (2007) reported that a vegetated bioretention cell made of fine sand/sandy loam/gravel media removed nitrate up to 93% while a non-vegetated bioretention cell made of the same media was a net nitrate exporter.

Nevertheless, much less is known about the composition of DON in urban stormwater runoff and its removal and fate in bioretention systems. Moreover, bioretention facilities release DON, likely due to dissolution and conversion of influent PON and vegetation residuals to DON. For instance, Li and Davis (2014) reported that a bioretention cell, located in College Park, MD, reduced PON concentration from 0.93 to 0.26 mg N/L, while raising DON concentration from 0.25 to 0.63 mg N/L. Overall,

incorporating a mechanism for DON removal from stormwater runoff can be highly beneficial to increasing the removal efficiency of TN.

Thousands of organic nitrogenous compounds, including proteins, peptides, amino acids, amino sugars, and heterocyclic nitrogen, exist in the environment (Paul, 2006). However, little information is available about the composition of DON in urban stormwater runoff (Taylor et al., 2005; Lusk and Toor, 2016). Due to lack of information on available organic nitrogen species in actual stormwater, dominant nitrogen species in soils and from plants were assumed as the most likely forms of organic nitrogen present in actual urban stormwater runoff. The major sources of organic nitrogen in urban areas are living and dead plants, natural organic compounds in soils, animal wastes, wastewater leakage, and fertilizers (Nannipieri and Smalla, 2006; Paul, 2006; Collins et al., 2010; Moore et al., 2011). TN in soil organic matter is estimated to consist of 40% proteinaceous materials (proteins, peptides, and amino acids), 5-6% amino sugars, 35% heterocyclic nitrogen and 19% ammonium nitrogen (Nannipieri and Smalla, 2006). Urea and ammonium are common compounds available in fertilizers, which are used to promote production of amino acids as the natural building blocks in plant bodies (Gowariker et al., 2009) . Protein and amino acids can move into soil from plant and animal residues (Stevenson, 1994; Nannipieri and Smalla, 2006). Although amino sugars are available in the structure of fungi and plants, it is generally assumed that the amino sugars in soil have microbial origin (Stevenson, 1994). Heterocyclic nitrogen occurs in residue of dead plants after combustion (Nannipieri and Smalla, 2006).

In nature, clays store organic nitrogen due to their adsorbing capability (Nannipieri and Smalla, 2006). Kaolinite and montmorillonite clay minerals are able to strongly adsorb positively-charged amino acids (40-80% removal); however, neutral and negatively-charged amino acids were not considerably adsorbed (Hedges and Hare, 1987). In addition, studies note that silica and zeolite are able to adsorb some types of amino acids through ion-exchange and hydrophobic interactions (Basiuk and Gromovoy, 1996; Krohn and Tsapatsis, 2005). Other studies have shown that humic acid can be adsorbed by zeolite, kaolinite, bentonite, chitosan, activated carbon, and xonotlite (Katsumata et al., 2003; Zhang and Bai, 2003; Salman et al., 2007; Maghsoodloo et al., 2011; Moussavi et al., 2011; Shaker et al., 2012). Activated carbon, alumina, silica, montmorillonite, kaolinite, and aluminosilicate were able to adsorb soil organic matter, which may contain nitrogen (Davis, 1982; Mayer, 1999; Ding et al., 2008; Qi and Schideman, 2008; Ando et al., 2010).

If bioretention media can adsorb and retain DON, the aerobic environment in bioretention cells may provide proper conditions for mineralization of influent DON to ammonium and nitrate (Equations 2-1 to 2-3; Rittmann and McCarty, 2001). In addition, retained DON can be taken up directly by plants. A study by Näsholm et al. (2009) confirms the ability of plants to directly acquiring amino acids from soil, while mentioning that it is not clear this process contributes to plant nitrogen nutrition. The generated ammonium can be managed by vegetation and nitrification using a layering approach. In addition, nitrate, which is generated from nitrification of ammonium, may be denitrified to nitrogen gas (Equation 2-4) shown with methanol as the electron

donor; Rittmann and McCarty, 2001) in an anoxic saturated zone of the bioretention cell.

$$Organic\ N + 4H_2O \rightarrow NH_4^+ + 4OH^- \quad (2\text{-}1)$$

$$NH_4^+ + \frac{3}{2}O_2 \rightarrow NO_2^- + 2H^+ + H_2O \quad (2\text{-}2)$$

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^- \quad (2\text{-}3)$$

$$\frac{5}{4}CH_2O + NO_3^- \rightarrow \frac{5}{4}CO_2 + \frac{1}{2}N_2 + \frac{3}{4}H_2O + OH^- \quad (2\text{-}4)$$

The goal of this study is to select long-lasting materials which are able to effectively adsorb DON expected in urban stormwater, such that these materials can be used as a component of a bioretention medium. In this regard, adsorption capacity and adsorption rate (kinetics) was investigated for eight selected organic nitrogenous compounds onto several adsorbents. High adsorption capacity will reduce the amount of adsorbent needed and high adsorption rate allows for more effective use of high-flow media.

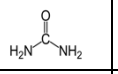
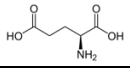
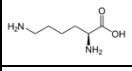
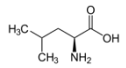
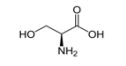
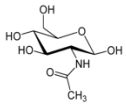
Materials and Methods

Selection of organic nitrogenous compounds for study

As discussed in the Introduction, hundreds of different organic nitrogenous compounds are available in the environment; from urea as a single chemical compound to categories of amino sugars, amino acids, and heterocyclic nitrogenous compounds to complex organic macromolecules. For this study, a few specific compounds were selected from categories of amino sugars, amino acids, heterocyclic nitrogen, and humic acid, which were employed to represent and reflect the properties of expected

common stormwater organic nitrogenous compounds. Water solubility, hydrophobicity/hydrophilicity, acidity/basicity, and extent of use/naturally availability were characteristics considered in selecting the organic nitrogenous compounds.

Table 2-2. Selected organic nitrogenous compounds for adsorption study (Lide, 2004; NIH, 2015)

Organic nitrogenous compound		**Chemical structure**	**Molar Mass (g/mole)**	**Total charge at pH 6-7**	**Log K_{ow}**	**pKa_1**	**pKa_2**	**pKa_3**	**Solubility at 25°C (mg/mL)**	**Manufacturer**
Urea	-		60.06	Neutral	-2.11	0.10	-	-	545	Fisher Scientific, Pittsburgh, Pennsylvania
Amino acid	L-Glutamic acid		147.13	Negative	-3.69	2.19	9.67	4.25	8.88	Alfa Aesar, Ward Hill, Massachusetts
	L-Lysine		146.19	Positive	-3.05	2.18	8.95	10.53	1000	Acros Organics, Geel, Belgium
	L-Leucine		131.17	Neutral	-1.52	2.36	9.63	-	21.5	Acros Organics, Geel, Belgium
	L-Serine		105.09	Neutral	-3.07	2.21	9.15	-	425	Fisher Scientific, Pittsburgh, Pennsylvania
Amino sugar	N-acetyl-D-glucosamine (NAG)		221.21	Neutral	-2.10	11.56	-	-	148	Alfa Aesar, Ward Hill, Massachusetts
Heterocyclic nitrogen	Pyrrole		67.09	Neutral	0.75	17.5	-	-	45	Acros Organics, Geel, Belgium
Humic acid	Aldrich humic acid (AHA)	-	-	-	-	-	-	-	-	Sigma Aldrich, St. Louis, Missouri

Urea was selected due to its uniqueness and widespread use in fertilizers. Among the most available amino sugars, N-acetyl-D-glucosamine (NAG), which is neutral and commercially available, was chosen for removal studies. Based on commercial availability, pyrrole was selected as representative of heterocyclic organic nitrogenous compounds. Four amino acids with different characteristics were chosen. The selected

organic nitrogenous compounds and some physical and chemical characteristics are presented in Table 2-2.

Selection and preparation of adsorbents

Adsorbents were selected based on their demonstrated ability to adsorb organic nitrogenous compounds or similar compounds such as natural organic materials and humic acids. In addition, basic bioretention materials, such as peat and quartz sand, were selected to examine their ability to adsorb DON (Table 2-3). Adsorbents were washed several times with deionized water to remove fines and dried in an oven at 110° C for 24 h.

Table 2-3. Selected adsorbents for DON adsorption study

Adsorbent	Type	Product/ Cat number	Size (mm)	Organic/ Mineral	Manufacturer
Activated carbon (AC)	Coal-based	Filtrasorb® 200	0.55-0.75	Organic	Calgon Carbon, Pittsburgh, Pennsylvania
	Coconut-based	OLC 12×40	0.55-0.75	Organic	Calgon Carbon, Pittsburgh, Pennsylvania
Charcoal	-	Hardwood lump	1.68-2.00	Organic	Royal Oak, Bradleyville, Missouri
Peat	-	-	1.68-2.00	Organic	Local vendor, Hyattsville, Maryland
Chitosan	-	C9213-500G	1.68-2.00	Organic	Sigma Aldrich, St. Louis, Missouri
Water treatment residual (WTR)	-	-	1.68-2.00	Mineral	Drinking Water Treatment Plant, Rockville, Maryland
Calcite	-	-	1.68-2.00	Mineral	Local vendor, Hyattsville, Maryland
Clay	Montmorillonite	24/48 LVM	0.30-0.71	Mineral	Agsorb, Chicago, Illinois
Silicate	Zeolite	BRZTM	0.25-0.60	Mineral	Bear River Zeolite, Preston, Idaho
	Quartz sand	Ottawa silica C-778 (20-30 grade)	0.5-1.0	Mineral	US Silica, Frederick, Maryland

Batch adsorption

The batch adsorption study was based on ASTM guideline D4646–03; 50-mL samples containing 0.5 grams adsorbent with a contact time of 24 hours were tested (ASTM, 2008). In some cases, in which the amount adsorbed was less than the TN detection limit, up to 3 grams adsorbent was used. To assure accuracy, duplicate samples were tested for each concentration. First, adsorbent and solution containing the adsorbate were added to 50-mL centrifuge tubes and mixed by end-over-end tumbling. After 24 hours, samples were filtered through 0.22-µm pore-size paper filters. Based on the information in Table 2-1, concentrations of total organic nitrogen in urban stormwater are near 1-2 mg N/L; however, the maximum limit for adsorption testing was selected as 5 mg N/L (initial DON concentration) to develop isotherms that cover lower ranges under the equilibrium conditions. Eight different concentrations were selected to cover the range up to 5 mg N/L. To mimic conditions of a typical urban stormwater, pH of the solution was adjusted to a range of 6-7 by 0.1 N NaOH or 0.1 N HCl. To control ionic strength, 0.01 M NaCl was used. The test was held at room temperature (22 ± 2°C).

Experiments were repeated for compounds that showed minimal signs of adsorption. However, the results of repeated tests were not significant enough to be considered as adsorption (equilibrium concentration, Ce < 0.1 mg N/L). The adsorbent mass for these adsorbents was increased up to 4 times of initial mass (0.5 g) for the repeated experiments.

Equilibrium adsorption capacity (q_e) in the batch adsorption study is calculated by using the Equation 2-5:

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (2\text{-}5)$$

where C_0 and C_e are initial and equilibrium concentrations of DON, respectively; m is the adsorbent mass, and V is the solution volume.

Freundlich models are used to gain an understanding of the adsorption behavior and surface heterogeneity. The Freundlich model can be represented as below:

$$q_e = K_F {C_e}^{1/n} \quad (2\text{-}6)$$

where K_F represents the adsorption capacity when the organic N equilibrium concentration (C_e) equals 1; n represents the degree of dependence of adsorption on equilibrium concentration.

To estimate the bioretention media performance and determine the adsorption capacity and lifetime of a specific adsorbent, Equations 2-7 and 2-8 are used:

$$q_e = \frac{Total\ mass\ of\ adsorbate\ in\ stormwater\ runoff\ (during\ bioretention\ operating\ period)}{Total\ mass\ of\ adsorbent\ used\ in\ bioretention} \quad (2\text{-}7)$$

$$q_e = \frac{D \times C \times t}{5\% \times \rho \times D_m} \quad (2\text{-}8)$$

where D represents annual precipitation depth; C represents the stormwater pollution concentration; t represents the bioretention operating lifetime; ρ represents the media bulk density; D_m represents bioretention media depth; q_e represents the media adsorption capacity at equilibrium. The 5% factor indicates that the bioretention facility

is sized at 5% of the impervious catchment area. Thus, catchment area can be cancelled in Equation 2-7 to reach Equation 2-8.

Finally, to compare the adsorbability of the selected organic nitrogenous compounds to actual stormwater nitrogen, a one-time batch adsorption study was completed for an actual water sample collected from the input to a bioretention site in College Park, MD. The bioretention site collects and treats stormwater runoff from 2800 m^2 of asphalt parking lot, roads, and concrete. The stormwater was analyzed for the concentration of nitrogen species and pH based on the methods presented in Table 2-4.

Table 2-4. Summary of analytical methods for water quality analysis

Parameters	**Analytical method**[1]	**Detection limit**
Total nitrogen (TN)	Standard Methods 4500NO_3^- (C)[2]	0.10 mg N/L
Ammonium nitrogen (NH_4^+-N)	Standard Methods 4500NH_3 (F)	0.02 mg N/L
Nitrate nitrogen (NO_3^--N)	Standard Methods 4500NO_3^- (C)	0.05 mg N/L
Nitrite nitrogen (NO_2^--N)	Standard Methods 4500NO_2^- (B)	0.01 mg N/L
Dissolved organic nitrogen (DON)	= TN – ([NH_4^+-N] + [NO_3^--N] + [NO_2^--N])	N/A
Total phosphorus (TP)	Standard Methods 4500P (B) and 4500P (E)	0.005 mg P/L

[1] APHA (2005)

[2] Bachmann and Canfield Jr, (1996); Valderrama, (1981)

Adsorption kinetics

In adsorption kinetics testing, 50-mL samples containing 0.5 grams of adsorbent and 1 mg N/L of adsorbate were used. In total, twelve samples were employed to test at different contact times. Adsorbent and solution containing adsorbate were added to ten 50-mL centrifuge tubes and mixed by end-over-end tumbling. The pH of the solution was adjusted to a range of 6-7 by 0.1 N NaOH or 0.1 N HCl and ionic strength

was 0.01 M NaCl. The test was held at room temperature (22 ± 2°C). For each designated contact time (0.25, 0.5, 1, 1.5, 2, 3, 5, 8, 12, and 24 hours), one tube was removed from the tumblers and filtered through a 0.22-µm pore-size paper filter.

The first order kinetics model, which had the best correlation with the results, is represented as (Lagergren, 1898):

$$q = q_e(1 - e^{-kt}) \quad (2\text{-}9)$$

where q_e and q are the amounts of adsorbate adsorbed at equilibrium and at time t, respectively, and k is the first order adsorption constant.

Water quality analysis

Samples were analyzed for nitrogen species including total nitrogen (TN), nitrate nitrogen (NO_3^--N), nitrite nitrogen (NO_2^--N), and ammonia nitrogen (NH_3-N) according to methods shown in Table 2-4.

The synthetic stormwater samples did not contain any particulate matter. Samples were filtered after the batch adsorption experiments. The actual stormwater sample was filtered for analysis and batch adsorption study. Thus, measured TN is equal to total dissolved nitrogen (TDN). DON was calculated by subtracting NO_3^--N, NO_2^--N, and NH_3-N from TN. If the sum of NO_3^--N, NO_2^--N, and NH_3-N equaled or exceeded the TN value, the DON concentration was recorded as zero. All nitrogen forms are reported as mg N/L to allow the proportion of TN to be calculated.

Adsorbent characterization

The surface analysis was completed only for coal activated carbon (AC), coconut-shell AC and montmorillonite, which were the materials that performed most

effectively in the batch adsorption experiments. The specific area of the adsorbents was measured based on N_2-isotherms using the BET model by using a Micromeritics® ASAP 2020 surface area and porosimetry analyzer. An ASAP 2020 analyzer was used to determine the total pore volume and average pore size of the adsorbents. The bulk and particle densities and porosity were determined according to guideline D7263-09 of ASTM (2009).

Results and Discussion

Characterization of adsorbents

The adsorbents characteristics are shown in Table 2-5. The specific surface areas of coal AC and coconut-shell AC are much greater than montmorillonite. Unlike the specific surface area, total pore volume of coal AC is smaller than coconut-shell AC but still larger than that of montmorillonite. The average pore size in coal AC and coconut-shell AC are smaller compared to montmorillonite which has average pore size 119.4 Å.

Table 2-5. Particle and media characterization of coal AC, coconut-shell AC, and montmorillonite

	Particle				**Media**	
Adsorbent	**Specific surface area (m^2/g)**	**Total pore volume (mL/g)**	**Average pore size (Å)**	**Particle density (g/L)**	**Bulk density (g/L)**	**Porosity (%)**
Coal AC	798	0.198	53.3	1503 ± 19	498 ± 19	57 ± 2
Coconut-shell AC	547	0.341	30.6	1314 ± 65	477 ± 13	64 ± 1
Montmorillonite	76	0.005	119.4	1926 ± 173	601 ± 11	69 ± 2

Adsorption capacity and isotherm models

As shown in Table 2-4, the detection limit of TN is 0.1 mg N/L which is equivalent to q_e = 0.01 mg N/g calculated by using Equation 2-5. Adsorption can be considered as negligible if q_e is lower than 0.01 mg N/g.

Quartz sand and calcite are widely available in nature. Sand, made of silica, is a basic material in constructing conventional bioretention systems. Humic acid contains carboxylic groups as amino acids do and can be adsorbed on inorganic materials (e.g., sand) as an important geochemical process (Jada et al., 2006). Based on the batch adsorption results, adsorption of glutamic acid, lysine, leucine, and NAG on the quartz sand was not detected, q_e < 0.01 mg N/g. Urea, however, was adsorbed on the sand at a very low capacity of 0.04 mg N/g such that it only occurred at high equilibrium concentration (C_e = 4.5 mg N/L). Hazen et al. (2001) noted that calcite is able to adsorb amino acids such as alanine and aspartic while other amino acids such as valine and lysine cannot be adsorbed. Based on the current study results, q_e was smaller than 0.01 mg N/g for all the selected organic nitrogenous compounds, which indicates minimal adsorption on calcite.

Water treatment residual (WTR), which is waste material generated from the drinking water treatment process, can adsorb 3.18 mg phosphate as P per kg media (O'Neill and Davis, 2012). The results show nitrogen release from WTR such that the adsorption capacity was negative and almost constant at -0.42 ± 0.2 mg N/g for all tested concentrations of leucine (0 to 5 mg N/L), such that the adsorption cannot be quantified. Peat, a natural organic material, is widely used in agriculture and some bioretention designs, and can naturally take up metals and cations (Bailey et al., 1999).

Peat released nitrogen such that the adsorption capacity was negative and almost constant at -0.34 ± 0.2 mg N/g for leucine. Another natural material, chitosan, which is made from crab and shrimp shells, has been noted to adsorb compounds such as dyes, heavy metals and organics (Wan Ngah et al., 2011). In this study, chitosan released high amounts of nitrogen, exceeding the maximum detection limit of the TN, 13 mg N/L, such that adsorption capacity was at most -1.3 ± 0.12 mg N/g.

Of the other adsorbents tested, montmorillonite, a clay, only significantly adsorbed lysine, which is a protonated amino acid. The adsorption of lysine onto the montmorillonite (a clay) was 0.07 mg N/g (C_e = 1 mg N/L), indicating a small amount of adsorption. The main adsorption mechanism of cations on clays is usually cation-exchange (Theng, 1974; Dashman and Stotzky, 1982). Because lysine has two positively-charged sites and one negatively-charged site at the tested pH range of 6-7, cation-exchange is a possible mechanism. Other studies support this hypothesis that positively charged amino acids are more readily adsorbed onto clay particles, compared to neutral or acidic counterparts (Dashman and Stotzky, 1982).

Activated carbon and charcoal are processed organic materials which are able to adsorb a wide variety of compounds, from toxic metals to organic pollutants (Bandosz, 2006). Although charcoal is more economical compared to the activated carbons, adsorption on the charcoal was not detected in this study (q_e < 0.01 mg N/g). On the other hand, coal AC and coconut-shell AC effectively adsorbed 6 out of 7 selected organic nitrogenous compounds. Adsorption data and isotherm models developed for these activated carbons are shown in Figure 2-1 and Figure 2-2. Freundlich constants (K_F and 1/n) are presented in Table 2-6.

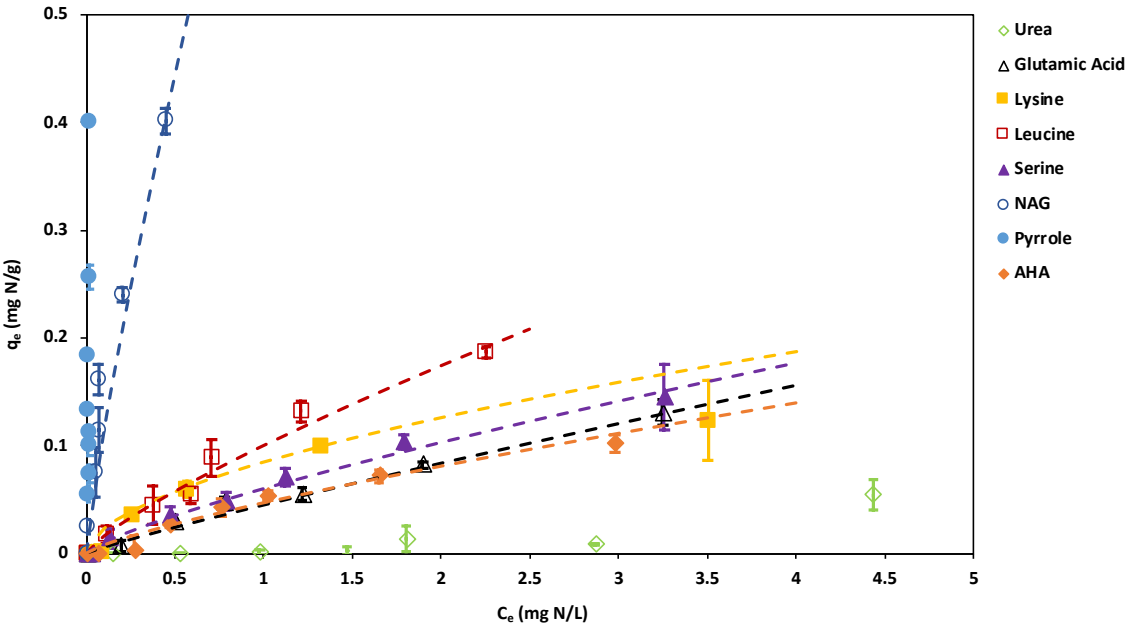


Figure 2-1. Isotherms for batch adsorption of the selected organic nitrogenous compounds on coal AC. The lines show Freundlich isotherm models. Background electrolyte = 0.01 M NaCl; pH = 6-7; Temperature = 22 ± 2°C; Contact time = 24 hours

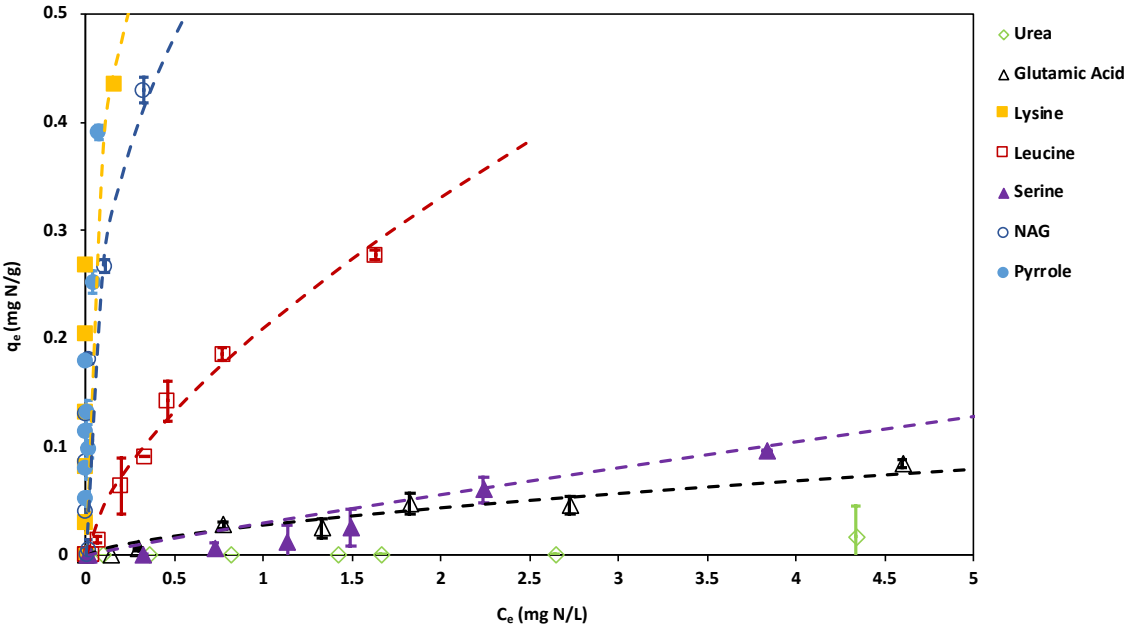


Figure 2-2. Isotherms for batch adsorption of the selected organic nitrogenous compounds on coconut-shell AC. The lines show Freundlich isotherm models. Background electrolyte = 0.01 M NaCl; pH = 6-7; Temperature = 22 ± 2°C; Contact time = 24 hours

Table 2-6. Model parameters obtained from fitting the experimental batch adsorption data with the Freundlich isotherm model for nitrogen in organic compound and for total organic compound.

	Coal AC					Coconut-shell AC				
Organic nitrogenous compound	**K_F (L/g)**	**1/n**	**R^2**	**Lifetime (day)**	**q_e^* (mg compound/L)[5]**	**K_F (L/g)**	**1/n**	**R^2**	**Lifetime (day)**	**q_e^* (mg compound/L)[5]**
Urea[1]	-	-	-	-	-	-	-	-	-	-
Glutamic acid	0.05	0.90	0.97	83	0.47	0.03	0.64	0.94	50	0.30
Lysine	0.09	0.57	0.87	157	0.89	0.77	0.30	0.70	1361	8.04
Leucine	0.10	0.80	0.96	184	0.94	0.21	0.65	1.00	371	1.97
Serine	0.06	0.78	0.97	111	0.45	0.03	0.90	1.00	53	0.23
NAG	0.80	0.85	0.80	1476	12.64	0.61	0.35	0.89	1078	9.64
Pyrrole[2]	-	-	-	-	-	-	-	-	-	-
AHA[3]	0.05	0.79	0.93	52	2.06	-	-	-	-	-
Average[4]	**0.22**					**0.33**				

[1] Due to low adsorbability of urea on both activated carbons, no isotherm could be developed.

[2] Despite high adsorbability, no isotherm model fits the batch adsorption data of pyrrole.

[3] Adsorption of AHA on coconut-shell AC was not tested.

[4] Urea, pyrrole, AHA are excluded for calculating average K_F (average q_e).

[5] q_e^* is the adsorption capacity of the whole compound (not only nitrogen) at C_e = 1 mg N/L.

Adsorption of the selected organic nitrogenous compounds on both coal AC and coconut-shell AC can be divided in five categories:

(1) Both activated carbons adsorbed pyrrole and NAG more than the other selected organic nitrogenous compounds. Pyrrole is highly adsorbable on both activated carbons to the point that it is difficult to fit the data to an isotherm model under the experimental conditions used. To compare adsorption of pyrrole on coal and coconut-shell ACs, adsorption capacities at C_e = 0.02 mg N/L are used. 0.02 mg N/L is the highest

equilibrium concentration at which experimental data are available for adsorption of pyrrole on both activated carbons, although that is lower than the TN detection limit (0.1 mg N/L). The adsorption capacities of coal and coconut-shell ACs for pyrrole are 0.4 and 0.19 mg N/g (C_e = 0.02 mg N/L), respectively. In addition, the adsorption capacities of coal and coconut-shell ACs for NAG are 0.80 and 0.61 mg N/g (C_e = 1.0 mg N/L), respectively. Thus, coal AC has greater capacity to adsorb pyrrole and NAG, which may be related to bigger pore size and higher density of coal AC compared to coconut-shell AC.

(2) The adsorption capacity of lysine on the coconut-shell AC is 0.77 mg N/g (C_e = 1.0 mg N/L), while the adsorption capacity on coal AC is only 0.09 mg N/g (C_e = 1.0 mg N/L). Sekar et al., (2004) reported that lead(II) cations are adsorbed by coconut-shell AC probably through electrostatic interaction (cation exchange). Lysine is positively charged at experimental pH (6-7), which may be the reason for higher adsorption capacity on coconut-shell AC compared to coal AC.

(3) Leucine was the strongest adsorbed after NAG and pyrrole, while less amounts of other amino acids were adsorbed. Leucine adsorption capacities on coal and coconut-shell AC are 0.10 and 0.21 mg N/g (C_e = 1.0 mg N/L), respectively. Leucine is a net neutral amino acid at pH 6-7. The net neutral charge may be the reason for higher adsorption of leucine compared to other selected amino acids.

(4) Glutamic acid, serine and AHA form the fourth category such that their adsorption capacity is less than 0.07 mg N/g (C_e = 1.0 mg N/L) on both types of AC. A study by Abe et al. (1983) noted that the adsorption capacity of CAL AC (Pittsburgh Activated Carbon Co.) for glutamic acid and serine is 0.33 and 0.02 mg N/g (C_e = 1.0

mg N/L), respectively. Activated carbons have non-uniform surface chemistry and pore structure which can vary significantly. Variation of activated carbons and environmental conditions such as ionic strength, temperature, and pH may explain the differences of adsorption capacity in this study and the Abe et al. (1983) study.

(5) As seen in Figure 2-1 and Figure 2-2, urea adsorption capacity on both activated carbons is less than 0.01 at C_e = 1 mg N/L, which makes urea the least adsorbable organic nitrogenous compound on both activated carbons. This low adsorption capacity may be due to its high solubility (545 mg/L at temperature = 20°C). Nonionic organic compounds like urea are usually adsorbed by partitioning between water and the organic adsorbents. High solubility reduces the chance of partitioning (Schwarzenbach et al., 2005). Due to low adsorbability of urea on both activated carbons, no isotherm model could be developed.

To determine which activated carbon has higher adsorption capacity and should be selected for further study, their average adsorption capacities (q_e) at C_e = 1 mg N/L are compared (Table 2-6). C_e = 1 mg N/L was selected because it is ten times greater than the TN detection limit (0.1 mg N/L, Table 2-4), but close to the stormwater DON concentration reported for College Park, MD (0.6 mg N/L, Table 2-1). It must be noted that the Freundlich constant (K_F) is equal to the adsorption capacity (q_e) at C_e = 1 mg N/L. The average adsorption capacity of coconut-shell AC was calculated as 0.33 mg N/g, which is greater than 0.22 mg N/g for coal AC (Table 2-6). Urea and pyrrole were excluded from the average calculation because the isotherms could not be fitted for them. AHA also was excluded, because it was not tested for coconut-shell AC. As seen, significant difference between adsorption capacities on coal and coconut-shell ACs for

lysine (0.09 and 0.77 mg N/g at C_e = 1 mg N/L, respectively) strongly affected the average adsorption capacity in favor of coconut-shell AC. If lysine is excluded as well, the average adsorption capacities of coal and coconut-shell AC are 0.25 and 0.22 mg N/g, respectively. As discussed before, coal AC can adsorb greater amounts of highly adsorbable compounds, such as pyrrole and NAG. In addition, batch desorption tests for the blank samples revealed that each gram of coconut-shell AC released 0.01 mg P, which may make coconut-shell AC a phosphorus exporter in bioretention systems. Consequently, coal AC was selected for further experimentation and recommended for use in bioretention media.

It must be mentioned that the concentrations of adsorbed nitrogenous compounds in this study are reported in terms of the concentration of nitrogen, not the entire organic compound. For instance, the adsorbed concentration of glutamic acid is 0.05 mg N/g at 1 mg N/L, which is equal to 0.47 mg/g as glutamic acid. q_e^* is the adsorption capacity of the whole compound (not only nitrogen) at C_e = 1 mg N/L, presented in Table 2-6. Although the adsorption capacities are different, the adsorption characteristics of the organic nitrogenous compounds can still be described using the same five categories discussed above.

Using Equation 2-8 to estimate the bioretention media performance, the lifetime of a specific adsorbent can be calculated. Values assumed were (i) typical annual rainfall for Washington DC Metropolitan Area (D) = 100 cm (40 in.); (ii) average stormwater DON = 1.0 mg N/L; (iii) depth of AC layer in the bioretention cell = 20.3 cm (8 in.), as will be discussed later; and (iv) the bulk densities (ρ) of coal and coconut-shell AC are 498 ± 19 and 477 ± 13 g/L, respectively. The longevity of coal and coconut-shell

AC for each selected organic nitrogenous compound is shown in Table 2-6. Activated carbons will last less than a year for most of the selected organic nitrogenous compounds. If the organic nitrogenous compounds available in actual stormwater act similar to pyrrole and NAG, the adsorption process can be considered highly effective in bioretention systems. Otherwise, coal AC will lose its adsorption capability in less than a year and biological processes should be considered instead of adsorption, which may include ammonification, nitrification, and denitrification (Equations 2-1 to 2-4) or plant uptake. Only adsorption of NAG on both activated carbons and adsorption of lysine and leucine on coconut-shell AC will last for more than three years. Adsorption capacities and longevity of both activated carbons for pyrrole were not estimated because no isotherm could be developed. However, its longevity is more than that for NAG because the adsorption capacities of coal (q_e = 0.40 mg N/g at C_e = 0.02 mg N/L) and coconut-shell ACs (q_e = 0.19 mg N/g at C_e = 0.02 mg N/L) for pyrrole greatly exceeded those of coal (q_e = 0.03 mg N/g at C_e = 0.02 mg N/L) and coconut-shell ACs (q_e = 0.16 mg N/g at C_e = 0.02 mg N/L) for NAG.

Removal efficiency and actual stormwater

While isotherms provide the ability to compare the adsorption capacity of an adsorbent, the removal efficiency can help with understanding the effluent quality. The removal efficiency for the three best adsorbents, montmorillonite, coal AC, and coconut-shell AC, at an initial DON concentration of 0.49 ± 0.08 mg N/L are compared in Figure 2-3. The adsorption of actual stormwater DON was also added to Figure 2-3. The TN concentration in actual stormwater was 1.34 mg N/L which includes 0.34 mg N/L PON, 0.63 mg N/L DON, 0.20 mg N/L nitrate, and 0.05 mg N/L nitrite such that

DON was the dominant nitrogen form in the stormwater. Actual stormwater DON is removed by more than 80% efficiency by both activated carbons.

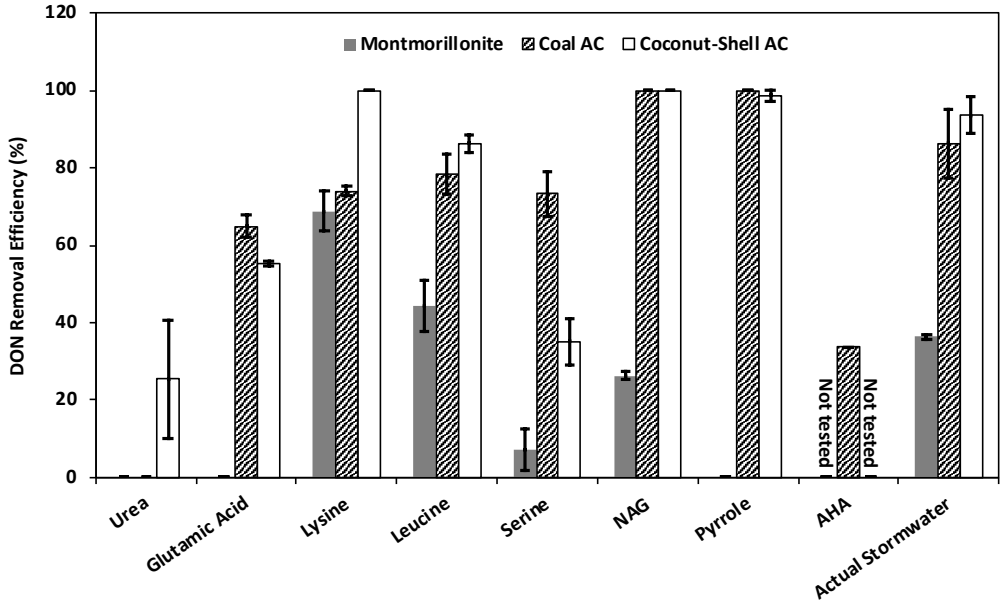


Figure 2-3. Comparison of removal efficiency of the selected organic nitrogenous compounds and real stormwater by coal AC, coconut-shell AC, and montmorillonite. For the selected compounds: Initial DON concentration (C_0) = 0.49 ± 0.08 mg N/L; Background concentration = 0.01 M NaCl; pH = 6-7; Temperature = 22 ± 2°C. For the actual stormwater: Initial DON concentration (C_0) = 0.63 mg N/L; pH = 5.7. Contact time = 24 hours

Comparing removal efficiency of the actual stormwater with batch study results at a similar concentration shows that DON adsorption from stormwater is similar to pyrrole or NAG. In addition, coal AC shows a more uniform removal efficiency for all the selected organic nitrogenous compounds. While coal AC has more than 64% removal efficiency for all the selected organic nitrogenous compounds (except urea and AHA), montmorillonite has less than 44% for all the selected compounds and coconut-shell AC less than 55% for four of the selected compounds.

Adsorption kinetics

Adsorption kinetics evaluations are important to quantify the time required to reach the adsorption equilibrium conditions and ultimate equilibrium adsorption capacity. This information is necessary to find the contact time required for DON removal in designing a bioretention system. As discussed previously, coal AC was selected for further studies. Results for the adsorption kinetics study for the selected compounds (except for AHA) on coal AC are shown in Figure 2-4. The adsorption kinetics experimental data for coal AC are well described by the first order kinetics model (Table 2-7).

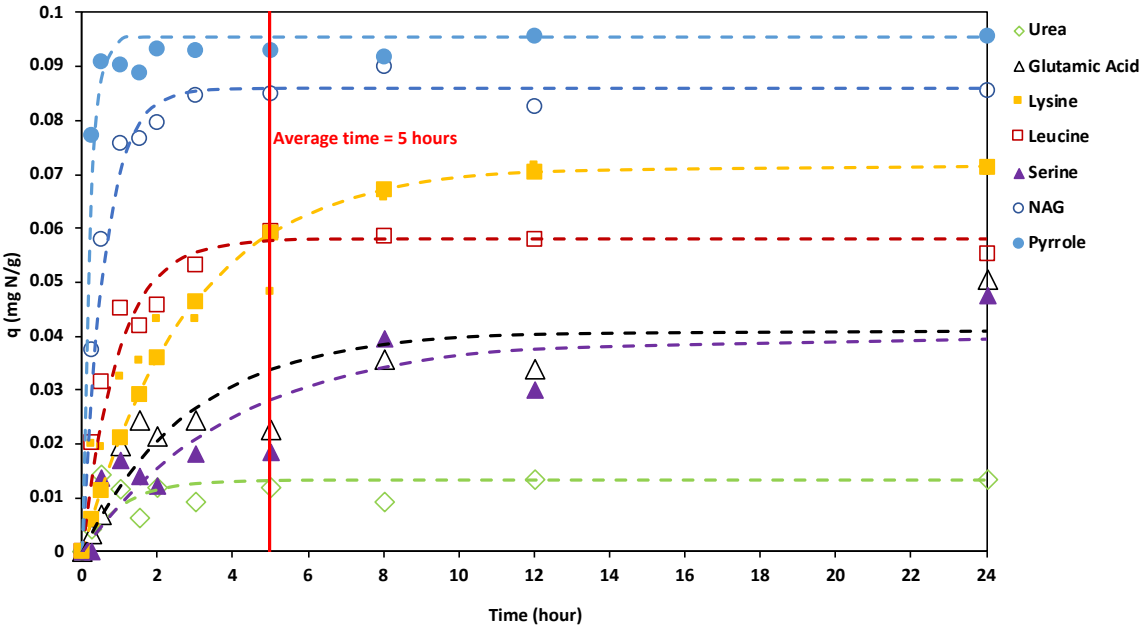


Figure 2-4. Adsorption kinetics of the selected organic nitrogenous compounds on the coal AC; the vertical line shows the average time to reach equilibrium adsorption capacity (qe). Initial DON concentration (C0) = 1 mg N/L; Background concentration = 0.01 M NaCl; pH = 6-7; Temperature = 22 ± 2°C

Similar to the coal AC isotherm (Figure 2-2), the adsorption kinetics follow nearly the same order for the selected organic nitrogenous compounds. Among the selected

compounds, not only does pyrrole have the best performance in the batch adsorption study, but also it has the fastest time, about one hour, to reach equilibrium adsorption capacity (q_e). The time to reach ultimate capacity is defined as the time at which the rate of change of adsorption capacity is less than 0.1 mg N/g-hr. The required time for each compound to reach the equilibrium adsorption capacity is shown in Table 2-7.

The second fastest compounds are NAG and urea at two hours, although urea still presents the lowest equilibrium adsorption capacity among the selected compounds. Leucine is slower and reaches adsorption equilibrium after three hours. The required contact time to reach the equilibrium adsorption capacity is more than eight hours for glutamic acid, lysine, and serine.

Table 2-7. Model parameters obtained from fitting the experimental DON adsorption rate data with the first order kinetics model (Equation 2-9), and the time to reach equilibrium adsorption capacity (q_e)

Organic nitrogenous compound	**k (hr^{-1})**	**q_e (mg N/g)**	**R^2**	**Time to reach q_e (hour)**	**q_1^* (mg N/g)[1]**	**Fraction of ultimate adsorption capacity, q_1^*/q_e**
Urea	1.00	0.013	0.98	2	0.008	0.62
Glutamic acid	0.35	0.041	0.84	8	0.012	0.29
Lysine	0.35	0.072	0.95	9	0.021	0.29
Leucine	1.05	0.058	0.95	3	0.038	0.66
Serine	0.25	0.040	0.75	10	0.009	0.23
NAG	1.70	0.086	0.99	2	0.070	0.81
Pyrrole	5.00	0.096	0.98	1	0.095	0.99
	Average	**0.058**	**-**	**5**	**0.036**	**-**

[1] q_1^* is the adsorption capacity at t = 1 hr.

The average time at which the ultimate adsorption capacity is reached for all the selected organic nitrogenous compounds is about 5 hours; this value is not practical for bioretention system design. To estimate a practical value for the contact time required

in bioretention systems, adsorption less than the equilibrium adsorption capacity must be accepted. If one-hour contact time (maximum adsorption capacity for pyrrole) is used as an acceptable contact time for all organic nitrogenous compounds, the average DON adsorption capacity will be 0.036 mg N/g, compared to 0.058 mg N/g at equilibrium. Depending on the similarities between organic nitrogenous compounds present in actual stormwater and the selected organic nitrogenous compounds in this study, the adsorption capacity of coal AC for actual stormwater can be greater or smaller than 0.036 mg N/g.

In Table 2-7, q_1^* is defined as the adsorption capacity of coal AC for 1 hour contact time. The lower q_1^*/q_e means longer lifetime of the adsorbent in a bioretention cell; however, it must be noted that the effluent water quality will not be improved to the extent possible if equilibrium cannot be reached. The q_1^*/q_e ratio for pyrrole and NAG is 99% and 88%, respectively, which means coal AC can achieve almost full adsorption capacity in a bioretention cell if actual stormwater DON shows adsorbability similar to pyrrole or NAG. As discussed before and shown in Figure 2-3, removal efficiency of DON from actual stormwater on the coal AC is near to the removal efficiency of pyrrole and NAG. Thus, designing the media filter for DON which can provide 1-2 hours contact time may be reasonable. The q_1^*/q_e ratio for the other compounds are less, varying from 66% to 23%.

Bioretention design for DON removal

Although 1.2 m (2.4 ft) is commonly recommended, the media depth selected for bioretention is dependent on type of pollutants targeted and media characteristics (Davis et al., 2009). A 20.3 cm-layer (8 inch-layer) of coal AC in bioretention is

suggested for removing DON from stormwater. This will allow enough space for other possible media materials for removing other pollutants, nutrients or other species of nitrogen. Typical bioretention infiltration rates vary from 1.3 (0.5) to 5.1 cm/h (2 in/hr) (Davis et al., 2009), which can be adjusted by media porosity and water head. A more rapid infiltration rate of 14.0 cm/h (5.5 in/hr) through a 20.3 cm (8 in) layer of coal AC with an average porosity of 57% will result in a contact time of about 0.83 hour. This is essentially equal to the required contact time (1 hour) for 1 mg N/L pyrrole to reach 99% of equilibrium adsorption capacity. The adsorption lifetimes of coal AC are calculated as up to 1476 days (4 years), which is the value for NAG (Table 2-6).

Unlike phosphorus, capture of nitrogen in bioretention systems is complicated due to the complex nitrogen cycle and high solubility of nitrate/nitrite, which make them less adsorbable to soil and bioretention media (LeFevre et al., 2015). A combination of biotic and abiotic (e.g., filtration and adsorption) processes should assist in enhancing the capture of nitrogen. In this regard, a four-layer bioretention cell is suggested to effectively address stormwater nitrogen. Although the goal of this study is not ammonium/nitrate removal, ammonium/nitrate existing in incoming stormwater or generated throughout bioretention media must be addressed in bioretention design.

The first top mixed-layer of sand and plant soil is located in the rhizosphere. This design will promote direct plant uptake of DON, nitrate, and ammonium. As discussed previously, DON can be adsorbed or transformed through ammonification and nitrification processes (Equations 2-1 to 2-3). Thus, a second top layer of coal AC is suggested to first adsorb DON and subsequently encourage mineralization of the captured DON, although highly soluble compounds such as urea may not be effectively

adsorbed. If deep-rooted plants are placed in bioretention, the second layer may also be part of the rhizosphere. Ammonium produced in the second layer, along with nitrate, will be either washed out from the second layer or taken up by the deep-rooted plants (Figure 2-5).

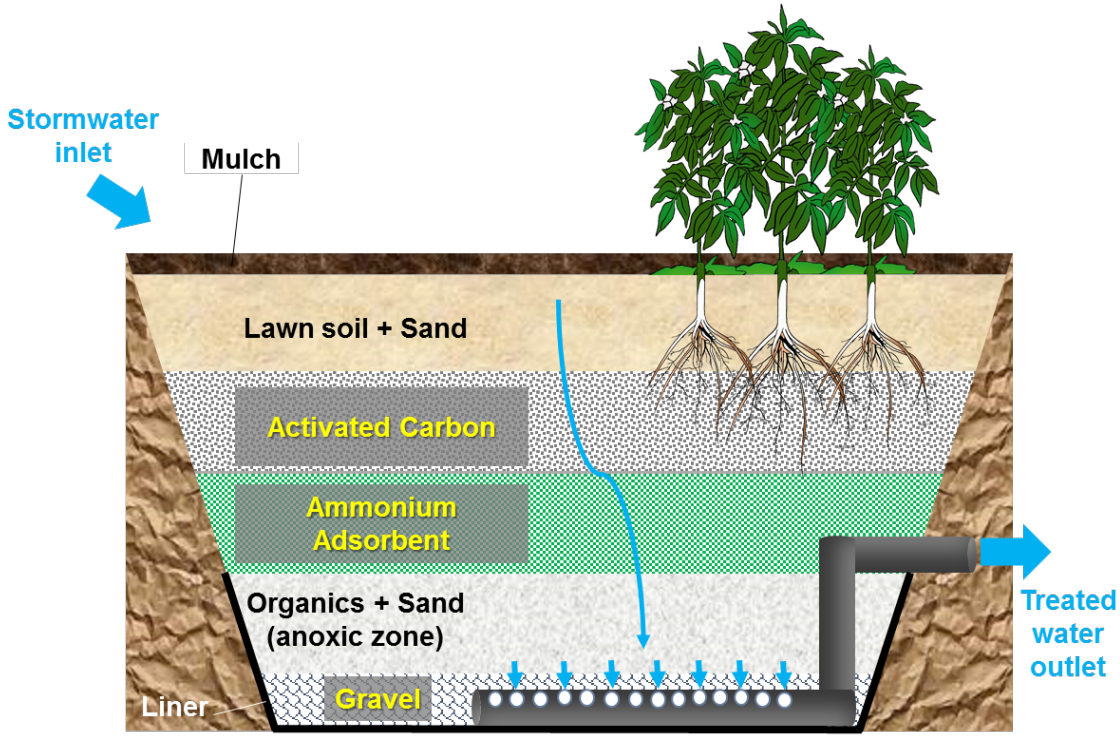


Figure 2-5. Nitrogen removal bioretention cell consisting of (1) a top layer of sand and plant soil to take up incoming nitrate and ammonium, (2) a second layer of sand and AC to adsorb DON and promote ammonification (3) a third layer to capture ammonium and promote nitrification (4) a bottom layer of sand/gravel and organic carbon source (e.g., newspaper or woodchips) to promote nitrate removal through denitrification. Plant uptake of ammonium, nitrate and DON may happen in the top and second layer.

To address ammonium washed-out from upper layers, a third layer of ammonium-adsorbing material is suggested to adsorb ammonium and possibly enhance its biotransformation to nitrate. Previous studies show that ammonium can be adsorbed to materials such as clays and zeolites through cation-exchange processes (Rožić et al.,

2000; Hedström, 2001). The nitrate, which is not captured by or washed out from the upper layers, can be removed through an anoxic layer (fourth layer). The fourth layer can be made of sand/gravel and an organic carbon source to promote nitrate removal through denitrification (Equation 2-4) (Kim et al., 2003; Peterson et al., 2015).

Conclusions

- Among the tested adsorbents, only coal AC and coconut-shell AC significantly adsorbed the selected organic nitrogenous compounds. The highest adsorption was observed for pyrrole and NAG. However, coal AC is considered for further studies and preliminary design of bioretention media for DON removal because coconut-shell AC released phosphorus during the adsorption test.

- The removal efficiency of actual stormwater DON (at initial DON concentration of 0.63 mg N/L) by both activated carbons was similar to removal efficiencies of pyrrole and NAG (at initial DON concentration of 0.49 ± 0.08 mg N/L). Consequently, adsorption capacity and kinetics for pyrrole and NAG on coal AC may be used for preliminary design of bioretention media for DON removal.

- The adsorption capacity of coal AC for pyrrole and NAG is recommended for designing bioretention systems targeting organic nitrogenous compounds which perform similar to pyrrole. Although the adsorption capacity of coal AC pyrrole is not known for C_e > 0.02 mg N/L, it is higher than that for NAG. An adsorption capacity of 0.71 mg N/g or greater is recommended for C_e = 1 mg N/L.

- Adsorption kinetics study suggests 1-2 hour contact time between DON and coal AC to reach 80-90% of ultimate adsorption capacity for highly adsorbable

compounds such as pyrrole and NAG, and about 60% or less for other tested organic nitrogenous compounds at initial DON concentration of 1 mg N/L. 1-hour contact time between adsorbent and DON is recommended for designing bioretention systems targeting organic nitrogenous compounds which perform similar to pyrrole and NAG.

- A 20.3 cm-layer (8 inch-layer) of coal AC is suggested for removing DON from urban stormwater. This design will allow enough depth for other possible filter materials removing other pollutants, nutrients or other species of nitrogen. An infiltration rate of 14.0 cm/h (5.5 in/hr) will result in a contact time of 0.97 hour between AC and pollutants.

Chapter 3: Column Adsorption of Compounds that Mimic Urban Stormwater Dissolved Organic Nitrogen

Abstract

Although nutrients are critical elements in aquatic ecosystems, excess nutrients can promote eutrophication in waterbodies. Bioretention systems are one of the measures to reduce nitrogen and phosphorus transferred by stormwater to local water resources. Bioretention systems are, however, not properly designed to remove dissolved organic nitrogen (DON) and may become a net DON exporter. Among eight organic nitrogenous compounds tested for continuous column adsorption on a media mixture of coal activated carbon (coal AC) + quartz sand, only pyrrole showed an appreciable adsorption performance; the breakthrough and exhaustion depths for pyrrole were 88 and 499 m (equivalent to 4.4 and 25.0 m simulated rainfall depth), respectively, at a fixed superficial velocity of 61 cm/h and fixed influent DON concentration of 1 mg N/L. The breakthrough depth for other organic nitrogenous compounds was less than 15 m and their exhaustion depths were between 44 and 191 m. Subsequent experiments on column adsorption of pyrrole using coal AC + quartz revealed that pyrrole was minimally affected by superficial velocity and its DON removal efficiency was > 91% for all tested superficial velocities (7 to 489 cm/h). Also, it was found that media bed height greater than 30 cm did not appreciably improve pyrrole exhaustion depth. The exhaustion depths for 15-, 30- and 50-cm bed heights were 499, 1042, and 1291 m (equivalent to 25.0, 52.1, and 64.6 m simulated rainfall depth), respectively. According to these results, adsorption processes can be employed for removing any part of stormwater DON behaving similarly to pyrrole. However, another strategy should be considered for removal of less adsorbable organic nitrogenous compounds; unintended ammonification in the current study suggests a possible approach for biological removal of stormwater DON.

Keywords: Bioretention, Rain Garden, Stormwater, Runoff, Organic Nitrogen, Column Adsorption

Introduction

Urban runoff can significantly impact the water quality in receiving water bodies (U.S. EPA, 1996, 1999). Various pollutants, including nutrients, nitrogen and phosphorus, are washed off and transferred by stormwater runoff from urban areas to valuable water resources. Excess nutrients promote eutrophication in receiving waters such as bays, rivers, and lakes (Stumm and Morgan, 2013).

Nitrogen wash-off from urban areas is a source-limiting process, meaning that stormwater runoff can remove most of the nitrogen from impervious surfaces even by low intensity rainfall (Miguntanna et al., 2013). Nitrogen is present in particulate and dissolved forms in stormwater (Li and Davis, 2014). Organic nitrogen, along with nitrate, forms the major part of the total dissolved nitrogen load in urban stormwater (Miguntanna et al., 2013). According to past studies, dissolved organic nitrogen (DON) forms 15-28% of total nitrogen (TN) while nitrate makes up 19-35%. Therefore, organic nitrogen removal is an important consideration for targeting nitrogen removal treatment design.

Bioretention, as a stormwater control measure (SCM), has been employed to reduce pollutants, including nutrients, heavy metals, and hydrocarbons from stormwater (Davis et al., 2009; Roy-Poirier et al., 2010; LeFevre et al., 2014). Particulate nitrogen can be effectively removed through sedimentation/filtration in bioretention systems (Li and Davis, 2014). Past studies have mainly concentrated on dissolved inorganic nitrogen removal (nitrate/nitrite and ammonium) while DON removal has been investigated less extensively (LeFevre et al., 2014), partly because of the lack of information on DON molecular characteristics. On the other hand, studies have shown

that some SMCs have higher DON concentrations in the discharge than in the influent, indicating that these systems failed to efficiently remove DON and became sources. Lusk and Toor (2016) found that stormwater DON increased from 1.09 to 1.85 mg N/L after flowing through a retention pond and bioavailable DON increased from 10.3% to 39.3%. In a bioretention system located in College Park, Maryland, stormwater particulate organic nitrogen (PON) decreased from 0.93 to 0.26 mg N/L while DON and nitrate increased from 0.25 to 0.63 mg N/L and 0.28 to 0.65 mg N/L, respectively (Li and Davis, 2014). These results reveal the necessity of effective adsorptive materials for stormwater DON removal in order to improve the design of bioretention systems and other SCMs.

The batch adsorption of eight different organic nitrogenous compounds on several adsorbents (coal activated carbon, coconut-shell activated carbon, charcoal, peat, chitosan, water treatment residual (WTR), calcite, montmorillonite, zeolite and quartz sand) was studied by Mohtadi et al. (2017). For most of the examined adsorbates and adsorbents, either the adsorption capacity was negligible, or nitrogen leached from the adsorbents. The results revealed that only two of the tested organic nitrogenous compounds (pyrrole and N-acetyl-D-glucosamine) were strongly adsorbed by Filtrasorb® 200 coal activated carbon. The adsorption capacities (q_e) of pyrrole and N-acetyl-D-glucosamine on coal activated carbon were 0.4 mg N/g (at equilibrium concentration, C_e = 0.02 mg N/L) and 0.71 mg N/g (at C_e = 1 mg N/L), respectively. Other organic nitrogenous compounds including leucine, lysine, glutamic acid, serine, and Aldrich humic acid were partially adsorbed on coal activated carbon (q_e < 0.1 mg N/L at C_e = 1 mg N/L) while the adsorption capacity for urea was negligible (q_e < 0.01

mg N/g). In this regard, coal activated carbon, which showed excellent adsorption of several examined organic nitrogenous compounds was chosen for further study on stormwater DON removal.

Batch experiments are static and tend to reach equilibrium or steady state conditions, which helps to estimate adsorption parameters in bulk solutions (Summers et al., 1992), but chemical equilibrium studies may overestimate the field adsorption capacities of adsorption media (Mateus and Pinho, 2010). Column adsorption mimics the transport of contaminants through adsorbents closer to field conditions such that it can assess the behavior of in-situ stormwater treatment systems (Richards and Bouazza, 2001). No performance data specifically related to column adsorption of stormwater DON were located, while many similar studies have examined removal of other types of pollutants in stormwater.

Activated carbon-amended columns were studied in the removal of organic compounds from actual stormwater (Kus et al., 2012; Sounthararajah et al., 2016; Björklund and Li, 2017); phenols, phthalates, and polychlorinated biphenyls from synthetic stormwater (Jaradat et al., 2010; Ulrich et al., 2015; Björklund and Li, 2017). Björklund and Li (2017) showed that the addition of activated carbon to a column increased bioretention media adsorption capacity of stormwater containing these organic compounds. The activated carbon thereby extended the bioretention media lifetime by approximately 10-20 years, indicating the importance of media adsorption capacity for stormwater treatment. In another study on removal of dissolved organic carbon from actual stormwater through an activated carbon-packed column, the removal efficiency dropped from 82.6% to 61.8% when superficial velocity increased

from 6.6 to 10 cm/h (Sounthararajah et al., 2016). The reduction in the removal efficiency appears to be due to reduction in the contact time between organic compounds and adsorption media as a result of increase in the velocity. Accordingly, adsorption capacity (extent of adsorption) and rate of adsorption (adsorption kinetics) are considered as two important factors controlling the functionality and exhaustion of bioretention media. To predict full-scale adsorption processes, these two factors must be determined (Summers et al., 1992).

In the current study, adsorption kinetics experiments were conducted for DON adsorption at different flowrates to estimate required superficial velocity, and accordingly, the required contact time between DON and column media. A higher superficial velocity means faster stormwater runoff infiltration, which is desirable in bioretention systems because more runoff volume can be treated from any given storm event. However, in the design of bioretention systems, the removal efficiency should not be sacrificed for high velocity. DON adsorption capacity experiments were performed using columns to determine adsorption curves and compare the results with batch adsorption experiments. A longer time to exhaustion indicates increased bioretention media lifetime, which reduces frequency of bioretention media maintenance/renewal need. The contact time also may vary by changing the media bed height at a fixed flowrate, which was also investigated in this study.

This study of DON column adsorption on activated carbon-amended media was conducted to:

- determine the breakthrough/exhaustion time for stormwater DON removal through adsorption processes based on column adsorption capacity experiments, and

consequently estimate the possible media lifetime in actual bioretention systems

- estimate the practical superficial velocity, and accordingly the contact time, required for stormwater DON removal through adsorption processes in actual bioretention systems based on column adsorption kinetics experiments
- find the practical media bed height required for a DON removal layer in bioretention systems by using results from column adsorption experiments with different media bed heights

Materials and Methods

Selection of organic nitrogenous compounds as adsorbates

In the current study, eight organic nitrogenous compounds were examined, including urea, four amino acids (l-glutamic acid, l-lysine, l-leucine, and l-serine), an amino sugar (N-acetyl-D-glucosamine, NAG), a heterocyclic nitrogenous compound (pyrrole), and Aldrich humic acid (AHA). All of these compounds were also examined by the authors in their previous study on DON batch adsorption; sources of these compounds can be found in Mohtadi et al. (2017).

Media mixture preparation and column setup

Glass columns were packed with a mixture of coal activated carbon (Calgon Carbon, Pittsburgh, Pennsylvania) and quartz sand (US Silica, Frederick, Maryland). According to the batch adsorption study by Mohtadi et al. (2017), coal activated carbon (AC) and coconut-shell AC demonstrated the best performance in DON adsorption among the tested adsorbents. Coal AC, however, holds larger specific surface area and average pore size compared to coconut-shell AC (Table 2-5), meaning that coal AC

would be a better choice for adsorption of large DON molecules. Higher particle density of coal AC, compared to coconut-shell AC (Table 2-5), can also be a sign of stronger structure. Additionally, coconut-shell AC released phosphorus during the adsorption testing (0.01 mg P/g). With consideration of the issues above, coal AC was selected for further studies on DON column adsorption.

To improve hydraulic conductivity, the coal AC was mixed with quartz sand such that ratio of sand to coal AC was 70:30 by mass. Both materials were washed several times with deionized (DI) water to remove fines and dust, then dried in an oven at 110°C for 24 h. The bulk and particle densities and porosities were determined according to ASTM (2009) guideline D7263-09. A Micromeritics® ASAP 2020 analyzer was used to determine the average pore size of coal AC. The characteristics of coal AC, quartz sand, and their mixture are shown in Table 3-1.

A total of 75 g of media mixture (22.5 g coal AC + 52.5 g quartz sand) was added to 15-cm long glass columns with 2.5-cm inner diameter. 30- and 50-cm long columns with the same inner diameter were packed for studying the effects of media bed height; 150 g (45 g coal AC + 105 g quartz sand) and 250 g (75 g coal AC + 175 g quartz sand) of the media mixture were added, respectively. The columns are made by Kimble-Chase (Rockwood, Tennessee). Peristaltic pumps and MasterFlex® tubing by Cole-Parmer Instrument Co. (Chicago, Illinois) were used to feed the columns at the desired flowrate. Up-flow was used in the columns to maintain saturation and avoid macropore channeling.

Table 3-1. Characteristics of coal AC, quartz sand and bed media mixture

Adsorbent	Product/ Cat number	Size (mm)	Average pore Size (Å)	Particle density (g/L)	Bulk density (g/L)	Porosity (%)
Coal AC	Filtrasorb® 200	0.55–0.275	53.3	1503 ± 19	498 ± 19	57 ± 2
Quartz sand	Ottawa silica C-778 (20-30 grade)	0.5-1.0	-	2533 ± 58	1603 ± 4	37 ± 1
Mixture of coal AC and quartz sand	-	-	-	2112 ± 56	1037 ± 2	51 ± 1

To inhibit the biodegradation of DON in the columns, all materials and devices were sanitized before use. Influent containers, columns, and tubing were washed with tap water, kept in a bleach bath (approximately 1:30 dilution – 120 mL Clorox® regular bleach in 3.8 L of water) overnight, and finally rinsed with deionized water several times.

Continuous column adsorption

DON removal was investigated in column studies with eight columns; one column for each organic nitrogenous compound. Based on a literature review, the concentration of total organic nitrogen in urban stormwater is approximately 1-2 mg N/L (Taylor et al., 2005; Li and Davis, 2014). Accordingly, the influent DON concentration and the ionic strength was set at 1 mg N/L and 0.01 M NaCl, respectively. Each column was fed by one organic nitrogenous compound at the fixed flowrate of 300 mL/h (superficial velocity 61 cm/h). The experiments were performed at room temperature (22 ± 2°C). To investigate the effects of media bed height on column adsorption, adsorption of pyrrole in three columns with heights of 15, 30, and 50 cm was studied.

Adsorption breakthrough/exhaustion curves were used to determine the adsorbent lifetime and maximum possible adsorbate removal. Column adsorption curves present effluent concentration as a function of applied depth (cumulative influent volume per unit area treated), which is calculated by

$$\text{applied depth} = \frac{Q\,t}{A} \tag{3-1}$$

where Q is column volumetric flowrate (mL/h); A is cross-sectional surface area of column (cm^2); and t is column adsorption duration (d). The applied depth is also represented as the rainfall depth. Assuming that the bioretention facility covers 5% of the impervious catchment area and 100% rainfall conversion to runoff, the rainfall depth was calculated by dividing the influent applied depth by 20.

Breakthrough and exhaustion points characterize the adsorption processes. The point where effluent concentration (C_{eff}) reaches 0.05 of influent adsorbate concentration (C_{inf}) is defined as the breakthrough point. Breakthrough continues as C_{eff} increases gradually up to $0.95C_{inf}$, which is termed the exhaustion point (Jain et al., 1997; Wang et al., 2007). A longer breakthrough time implies a longer time for an adsorbent to reach its effective capacity for an adsorbate. Because the influent DON concentration was nominally 1 mg N/L, the effluent breakthrough and exhaustion DON concentrations were 0.05 and 0.95 mg N/L, respectively.

Equation 3-2 describes the calculation of adsorption capacity using adsorption column parameters:

$$q = \frac{total\ mass\ of\ substance\ adsorbed}{total\ mass\ of\ adsorbent} = \frac{\int_0^t (C_{inf} - C_{eff}) \times Q\ dt}{m} \quad (3\text{-}2a)$$

$$\approx \frac{C_{inf} \times Q \times t_d}{m} \quad (3\text{-}2b)$$

where q is the adsorption capacity (mg/g); C_{inf} and C_{eff} are the influent and effluent adsorbate concentrations (mg/L), respectively. Q is column volumetric flowrate (mL/h); t_d is adsorption duration until column exhaustion (h); and m is the total mass of column adsorbent (g). If C_{eff} is assumed to be zero until adsorption media exhaustion, Equation 3-2b can be derived from Equation 3-2a at constant Q.

Equation 3-2a is employed to calculate the column adsorption capacity and compare it with the adsorption capacity obtained from batch adsorption experiments. Equation 3-2b can be used to predict the exhaustion depth from batch experiments, then compared with the experimental column exhaustion depth.

Column adsorption kinetics

To estimate the contact time required for effective DON removal, a column adsorption kinetics study was conducted. The media bed height was 15 cm and the test was held at room temperature (22 ± 2°C). Similar to column adsorption capacity experiments, the influent DON concentration and the ionic strength were fixed at 1 mg N/L and 0.01 M NaCl, respectively.

The adsorption kinetics experiments were performed for adsorption of the eight organic nitrogenous compounds on the media mixture of coal AC + quartz sand at varied flowrates (Table 3-2). The equivalent superficial velocity, empty-bed contact time, and true contact time are also shown in Table 3-2. Each organic nitrogenous

compound was examined with one separate column, and the superficial velocity was gradually increased from 7 to 489 cm/h. The columns were run at each velocity for three times of the empty-bed contact time (EBCT). The true contact time (CT) and EBCT are calculated by

$$EBCT = \frac{L}{v_s} \tag{3-3}$$

$$CT = \frac{L}{v_p} = \frac{L}{v_s/\emptyset} = \frac{L}{v_s} \times \emptyset \tag{3-4}$$

where L is media bed height; $\emptyset$ is media porosity; v_p is pore velocity; and v_s is superficial velocity.

Table 3-2. Varied flowrates, equivalent superficial velocities and contact times for adsorption kinetics experiment

Step	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Flowrate (mL/h)	33	90	165	300	615	1140	1800	2400
Superficial velocity (cm/h)	7	18	34	61	125	232	367	489
Empty-bed contact time (min)	134	49	27	15	7.18	3.87	2.45	1.84
True contact time (min)	69	25	14	7.57	3.69	1.99	1.26	0.95

Analytical methods

The focus of this study was on removal of dissolved organic nitrogen, and accordingly the synthetic stormwater samples did not contain any particulate matter. It is expected that any particulate matter would be filtered from the stormwater in upper media layers. Each sample was tested for total nitrogen (TN), ammonium nitrogen (NH_4^+-N), and nitrate nitrogen (NO_3^--N). Nitrite nitrogen (NO_2^--N) was measured in random samples; because nitrite was less than the detection limit of 0.01 mg N/L, it was considered as negligible in the calculations. DON was calculated by subtracting

NO_3^--N and NH_4^+-N from TN. The analytical methods used in this study are presented in Table 3-3. All nitrogen forms are reported as mg N/L.

Table 3-3. Summary of analytical methods for water quality analysis

Parameters	Analytical method	Detection limit
Total nitrogen (TN)	Shimadzu TOC/TN analyzer (TOC-L + TNM-L series)	0.05 mg N/L
Ammonium nitrogen (NH_4^+-N)	Standard Methods 4500NH_3 (F)[1]	0.02 mg N/L
Nitrate nitrogen (NO_3^--N)	Standard Methods 4500NO_3^- (C)[1]	0.05 mg N/L
Nitrite nitrogen (NO_2^-N)	Standard Methods 4500NO_2^- (B)[1]	0.01 mg N/L
Dissolved organic nitrogen (DON)	= TN – ([NH_4^+-N] + [NO_3^--N])	N/A

[1] APHA (2005)

The samples were collected approximately daily for all columns except pyrrole. For pyrrole, sampling was made approximately daily for first two weeks, then once per 2-3 days. The collected samples were stored in centrifuge tubes and kept cold at 4°C. All laboratory devices and analytical procedures were calibrated before use. Six standards were used for every analytical procedure and R-squared for the standard curves was not less than 0.95. Some samples were randomly reanalyzed to ensure variation of two measurements did not exceed 10%; otherwise, all samples were reanalyzed for that run. All glassware used in water quality analysis were acid-washed before use.

Results and Discussion

Continuous column adsorption

Figure 3-1 shows effluent TN changes as a function applied water depth for continuous column adsorption of eight organic nitrogenous compounds on a mixture of coal AC + quartz sand at a superficial velocity of 61 cm/h (contact time 15 min);

influent TN concentration (= influent DON concentration) was 1 mg N/L. Because of the significant difference between results of pyrrole and the other seven compounds, two diagrams are used separately to present column adsorption results. Despite all efforts done, as explained in the Materials and Methods section, ammonification could not be eliminated and it affected the adsorption process to some extent. Due to ammonification, the effluent contained two primary components (DON and ammonium), while the influent solution contained only DON.

According to Figure 3-1, generally, as the influent depth and loading of TN progressed, the effluent TN increased, indicating reduction in the media adsorption capacity. AHA and leucine columns reached their adsorption capacities (exhaustion) after receiving about 44 and 191 m of influent, respectively. The exhaustion depths for urea, glutamic acid, lysine, serine and NAG were between 44 and 191 m. The breakthrough for all compounds could not be determined because it happened after only a few hours, less than 15 m, while the sampling was performed daily. Unlike the compounds discussed above, pyrrole showed much stronger adsorption performance such that its breakthrough and exhaustion depths were 88 and 499 m, respectively. Equivalent simulated rainfall depths for breakthrough and exhaustion of pyrrole were calculated as 4.4 and 25.0 m, respectively. The pyrrole effluent concentration after the column exhaustion was slightly more than influent concentration of 1 mg N/L, which may indicate some pyrrole desorption after exhaustion.

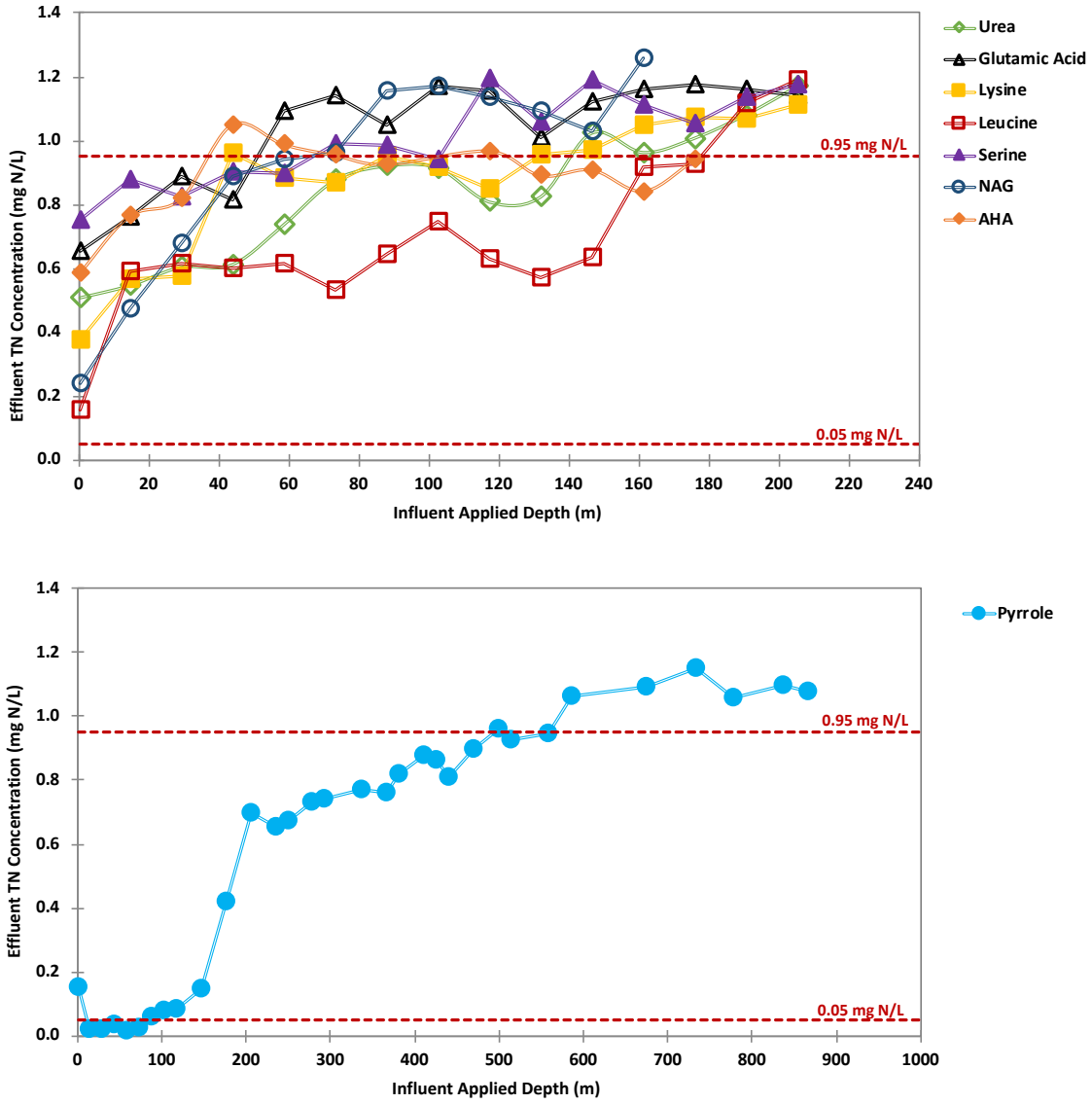


Figure 3-1. Column adsorption of the selected organic nitrogenous compounds on the media mixture of coal AC + quartz sand. Media bed height = 15 cm; Background electrolyte = 0.01M NaCl; Temperature = 22 ± 2°C; Superficial velocity = 61 cm/h; Influent DON concentration = 1 mg/L

A summary of the results from the current study, continuous column adsorption, alongside the results from the previous batch adsorption study conducted by Mohtadi et al. (2017) at pH = 6-7 and room temperature (22 ± 2°C) is shown in Table 3-4. Also, using the batch adsorption results and Equation 3-2b, the exhaustion depth was

estimated for all the examined compounds. It must be noted that isotherm expressions could not be obtained for urea and pyrrole in the batch adsorption study and the batch adsorption capacity could not be calculated accordingly. Because the batch adsorption capacity of urea on coal AC was less than 0.01 mg N/g (at equilibrium concentration, C_e = 1 mg N/L), the batch adsorption capacity for urea is considered as 0.01 mg N/g. Also, the batch adsorption capacity for pyrrole is considered as 0.4 mg N/g, observed at the maximum batch C_e for pyrrole (0.02 mg N/L). The column breakthrough and exhaustion depths were determined from Figure 3-1 and added to Table 3-4. The column adsorption capacities on coal AC were calculated by using Equation 3-2a.

According to Table 3-4, the column exhaustion depths and adsorption capacities are much greater than those estimated from the batch results, with the exception of NAG. The different result for NAG appears to have resulted from a clear thin film that formed on the column media surface. The clear film was probably hydrogel because NAG is one of the major components that form hydrogel in nature, e.g., chitosan, and has been used to make synthetic hydrogel (Park et al., 2002; Qiu et al., 2011). This film possibly blocked the coal AC surface exposure to NAG molecules. For the other compounds, the column adsorption capacity is 3 to 14 times those of the batch results while it is 76 times that of the batch results for urea (Table 3-4). Because the column and batch results for pyrrole are presented at two different equilibrium concentrations, the pyrrole results are not comparable.

Table 3-4. Comparison of the results from column and batch (Mohtadi et al., 2017) studies

Organic nitrogenous compound	Column (at C_e = 1.0 mg N/L)			Batch (at C_e = 1.0 mg N/L)	
	Breakthrough depth (m)	Exhaustion depth (m)	Adsorption capacity (mg N/g)	Adsorption capacity (mg N/g)	Estimated exhaustion depth (m)
Urea	< 15	147	0.76	0.01	0.5
Glutamic acid	< 15	59	0.21	0.05	2.1
Lysine	< 15	88	0.47	0.09	3.9
Leucine	< 15	176	1.40	0.10	4.6
Serine	< 15	73	0.20	0.06	2.8
NAG	< 15	73	0.45	0.80	36.7
Pyrrole	88	499	4.62	0.40*	18.4*
AHA	< 15	44	0.19	0.05	2.2

* at C_e = 0.02 mg N/L; pyrrole results from the batch and column experiments are reported at two different C_e and cannot be directly compared.

The focus of this study was specifically on adsorption of stormwater DON; however, ammonification occurred in all the adsorption columns (except pyrrole) despite the prevention measures taken. Ammonium was detected the first time in all the samples collected at influent applied depth of 15 m. The ammonification possibly resulted in bioregeneration of the coal AC adsorption sites and as a result, the column adsorption capacity for all the compounds (except NAG) are greater than the batch adsorption results. Bioregeneration of activated carbon saturated by organic compounds has been reported by others (DeWalle and Chian, 1977; Chudyk and Snoeyink, 1984; de Jonge et al., 1996; Lee and Lim, 2005).

At the end of the experiment, the effluent ammonium concentration for three compounds, serine, glutamic acid and leucine, were between 0.27 and 0.69 mg N/L.

Urea, lysine, NAG, and AHA had lower effluent ammonium concentrations (< 0.21 mg N/L). Pyrrole, however, was an exception and its biotransformation to ammonium was negligible such that the effluent ammonium concentration stayed less than the detection limit (0.02 mg N/L) during the experiment. The rigid chemical structure of heterocyclic aromatic compounds (e.g., pyrrole) makes them less biodegradable (Subbaramaiah et al., 2013; Singh et al., 2015; J. Li et al., 2016). The unintended ammonification may improve DON removal in addition to adsorption processes, which will be discussed in Chapter 4.

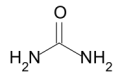
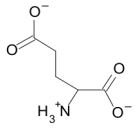
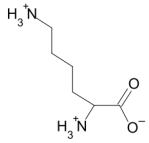
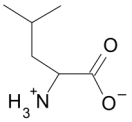
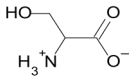
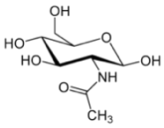
Assuming that the actual stormwater contains compounds similar to pyrrole with average DON = 1.0 mg N/L, where typical annual rainfall depth for the Washington DC Metropolitan Area is 100 cm, a 15-cm layer of the adsorption media mixture (coal AC + quartz sand; 70:30 by mass) with superficial velocity of 61 cm/h could last for ($\frac{4.4\ m}{1\ m/yr}$ =) 4.4 years if the breakthrough depth is applied and ($\frac{25.0\ m}{1\ m/yr}$ =) 25 years if considering the exhaustion depth. Compared to other studies on bioretention media removing heavy metals and phosphorus from stormwater for the Washington DC Metropolitan Area, the media lifetime for pyrrole is very low at the breakthrough point and is moderate at the exhaustion point. The lifetime of sandy loam soil (61 cm) topped with a 2.5 cm layer of mulch, to remove stormwater heavy metals (including copper, lead, and zinc) was determined at about 15-20 years (Davis et al., 2003). According to Yan et al. (2017), high-flow bioretention media (HFM, sand), WTR (water treatment residue)-amended HFM, and partially hydrolyzed aluminum-WTR-amended HFM was

predicated to last for 3.8, 19, and 41 years, respectively, in removing myo-inositol hexakisphosphate, an organic phosphorus compound, from synthetic stormwater.

Review of possible adsorption mechanisms

By knowing the physical/chemical properties of coal AC and the examined compounds, the results and possible mechanisms involved in their adsorption process can be discussed. The possible predominant form for each examined organic nitrogenous compound was determined based on the compound's pK_a and its effluent pH (Table 3-5). Filtrasorb® 200 coal AC is known as a H-type activated carbon (Chen and Lin, 2001a; Chen and Wu, 2004a; Corapcioglu and Huang, 1987). H-type carbons are hydrophobic in nature, tend to have a high pH_{zpc}, and become positively-charged upon exposure to water (Cooney, 1998; Rinklebe et al., 2016; Grumezescu and Holban, 2019). The predominant surface functional groups in H-type carbons are acidic groups such as lactone, quinone, phenolic hydroxyl, and carboxyl (Ishizaki and Martí, 1981), which can adsorb cations and aqueous hydrogen ions. Surface analysis on DI-washed Filtrasorb® 200 coal AC suggested carboxyl, phenol, ether, and lactone as the predominant surface functional groups (Chen and Wu, 2004). The pH_{pzc} of Filtrasorb® 200 coal AC was found to be 7.0 to 7.2 (Chen and Lin, 2001a, 2001b; Yang et al., 2007). According to Chen and Lin (2001b) and based on the experimental effluent pH values presented in Table 3-5, Filtrasorb® 200 coal AC surface charge density would be approximately +25 to -10 C/cm^2, meaning that the coal surface was near neutral charged while the adsorption columns were running. Adsorption of the organic nitrogenous compounds and possible mechanisms involved can be discussed in five categories:

Table 3-5. Chemical properties of each organic nitrogenous compound

Organic nitrogenous compound		Log K_{ow}*	pK_a*				Experimental effluent pH	Predominant form	
			1	2	3	Origin			
Urea	-	-2.11	0.10		-	$pK_{a,1}$: OH^+ (protonated form)	5.93 ± 0.47	Neutral polar	
Amino acid	Glutamic acid	-3.69	2.19	9.67	4.25	$pK_{a,1}$: COOH $pK_{a,2}$: NH_2 $pK_{a,3}$: Side chain	5.50 ± 0.59	Acidic polar	
	Lysine	-3.05	2.18	8.95	10.53		6.38 ± 0.21	Basic polar	
	Leucine	-1.52	2.36	9.63	-		6.04 ± 0.63	Neutral non-polar	
	Serine	-3.07	2.21	9.15	-		6.37 ± 0.24	Neutral polar	
Amino sugar	NAG	-2.10	11.56	-	-	$pK_{a,1}$: NH	6.09 ± 0.37	Neutral polar	
Heterocyclic nitrogen	Pyrrole	0.75	17.5	-	-	$pK_{a,1}$: NH	5.93 ± 0.53	Neutral non-polar	
Humic acid	AHA	-	1.6†	-	-	-	8.25 ± 0.28	Negatively -charged polar	-

* NIH (2019)
† pH_{zpc} (Zhang and Bai, 2003)

(a) Urea is a neutral polar compound in water. Adsorption of urea on soil was found to be due to hydrogen bonding between polar urea and oxygens of functional groups of soil humic substances (Chin and Kroontje, 1962; Mitsui and Takatoh, 1963). The slightly positive-neutral surface of coal AC at pH of 5.93 ± 0.47 might reduce the chance of hydrogen bonding or Van der Waals forces between urea and the AC surface.

According to Table 3-5, the batch adsorption capacity of urea on coal AC was very low, less than 0.01 mg N/g (at C_e = 1 mg N/L); however, the current study returned much higher column adsorption capacity (0.55 mg N/g), which may be due to the presence of the sand in the column adsorption media mixture. Mohtadi et al. (2017) found that urea was also adsorbed on the quartz sand at a capacity of 0.04 mg N/g at C_e = 4.5 mg N/L.

(b) As seen in Table 3-5, the effluent pH for glutamic acid, lysine, leucine, and serine ranged from 5.50 ± 0.59 to 6.38 ± 0.21 less than the reported pH_{pzc} of 7-7.2. Accordingly, the coal AC surface would be slightly positive/neutral. At this pH range, glutamic acid is anionic and lysine is cationic, while leucine, and serine would be non-polar and polar neutral zwitterions, respectively. The neutral surface of coal AC would reduce the chance of ionic or hydrogen bonding for adsorption of these amino acids. Among the tested amino acids, leucine was the only compound with non-polar characteristics and has the highest Log K_{OW} among the examined amino acids, which would possibly help leucine to partition to the coal AC-water interface. In general, activated carbon can effectively adsorb non-polar compounds, while adsorption capacity is poor for polar substances (Faust and Aly, 1998; Ying, 2001; Bansal and Goyal, 2005; Xie, 2013). As a result, leucine showed better adsorption results among the tested amino acids (Table 3-5).

(c) NAG becomes a neutral polar compound upon introduction to water. At pH of 6.09 ± 0.37, the coal AC surface would be nearly neutral or slightly positively-charged. CH-π interactions can be developed between the glucose unit of organic compounds and carbon surfaces (Dornath, 2016; Kobayashi et al., 2016). NAG includes a glucose

unit in its structure, which makes CH-π interactions a possible adsorption mechanism. Although the column adsorption of NAG was adversely affected, probably by thin film formation, batch adsorption study has shown appreciable adsorption capacity, 0.80 mg N/g at C_e = 1 mg N/L (Table 3-5).

(d) Pyrrole is a type of heterocyclic compound. Heterocyclic compounds have been reported to be adsorbed on carbon surfaces through π interaction (Yu et al., 2011; Qu et al., 2016). Also, log K_{ow} of pyrrole is positive which may encourage pyrrole to partition onto the adsorbent surface. Positive log K_{ow} and π interactions are possible reasons for the high adsorption capacity of pyrrole on coal AC (4.24 mg N/g at C_e = 1 mg N/L) and its large column exhaustion depth (449 m) among the examined compounds (Table 3-5).

(e) Adsorption of humic acids on activated carbons is dependent on the physico-chemical characteristics of both humic acids and activated carbons. The adsorption of humic acid on activated carbon was reported to be strongly pH dependent; pH decrease from 6.7 to 2 increased humic acid adsorption from 50% to 80% (Chen and Wu, 2004b). Zhang and Bai (2003) reported a pH_{pzc} of 1.6 for AHA, such that AHA surface charge was negative at pH > 1.6, due to deprotonation of carboxylic and phenolic groups. The coal AC surface charge in the AHA column would be slightly negative/zero at pH 8.25 ± 0.28 (> pH_{zpc} of 7-7.2). Such a condition would increase the chance of electrostatic repulsion between AHA and the coal AC surface. Different types of humic acids have been found to have hydrodynamic radii in the range of 2.42-12.8 nm (Österberg et al., 1993; Kawahigashi et al., 2005; Kawahigashi et al., 2011). The coal AC average pore size in the present study was determined as 5.33 nm (Table 3-5). Therefore, it is

possible that a part of the activated carbon pore volume is not accessible to large humic acid molecules, as also reported by Daifullah et al. (2004) and Lin et al. (2012). Chen and Wu (2004b) have also reported the blockage of activated carbon porous structures by humic acid macromolecules, resulting in decrease in the effective specific surface area. Cumulatively, these conditions can lower the adsorption capacity of AHA on coal AC, as found in both column and batch adsorption studies (Table 3-5).

Effect of media bed height on column adsorption

The column adsorption curves of pyrrole developed for bed heights of 15, 30, and 50 cm at 61 cm/h and 1 mg N/L influent DON are given in Figure 3-2. The breakthrough and exhaustion depths of these columns as well as their adsorption capacities are also compared in Figure 3-3. The gradient of the adsorption curves for these three media bed heights were slightly different. The breakthrough depths for 15-, 30- and 50-cm bed heights were 88, 147, and 147 m (equivalent to 4.4, 7.4, and 7.4 m simulated rainfall depth), respectively. The exhaustion depth, however, was more sensitive to media bed height changes; 15-, 30- and 50-cm columns showed exhaustion depths of 499, 1042, and 1291 m (equivalent to 25.0, 52.1, and 64.6 m simulated rainfall depth), respectively. The column adsorption capacity decreased with increase of media bed height; 5.12, 4.30, and 3.88 mg N/g, respectively for 15-, 30- and 50-cm columns.

Longer bed height means more adsorbent mass, larger contact area, and greater number of adsorption sites (Goel et al., 2005; Crini and Badot, 2011; Chowdhury et al., 2013). If the adsorption capacity is assumed to be fixed, increase in the adsorbent mass should linearly increase the exhaustion depth according to Equation 3-2a. However,

both exhaustion and breakthrough depths non-linearly correlated with the media bed height. Beyond a specific bed height, other studies also found that the adsorption curve did not show an appreciable change in effluent concentration with increase in bed height (Mondal, 2009; Dutta and Basu, 2014). This appears to be due to less probability of contact between adsorbate and adsorbent under flow conditions in fixed-bed mode compared to stirred batch mode (Al-Qodah and Lafi, 2003; Tan et al., 2008).

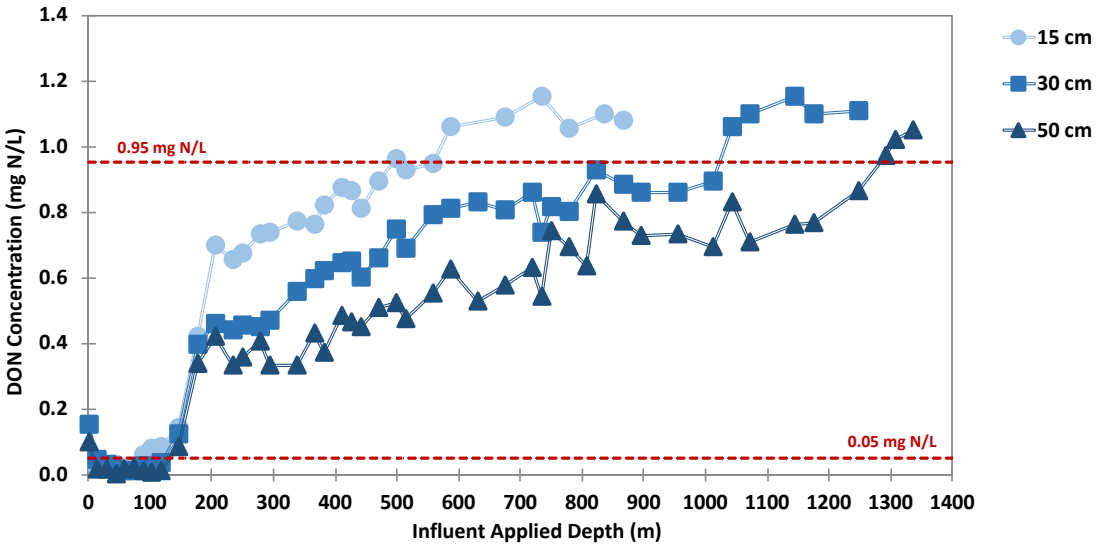


Figure 3-2. Column adsorption of pyrrole on the media mixture of coal AC + quartz sand for three bed heights (15, 30, and 50 cm). Background electrolyte = 0.01M NaCl; Temperature = 22 ± 2°C; Superficial velocity = 61 cm/h; Influent DON concentration = 1 mg N/L.

The column exhaustion depth increased by approximately 32 m for every centimeter increase in bed height between 15 and 30 cm, while it increased only 12.5 m between 30 and 50 cm. Because the impact of exhaustion depth is appreciably declining beyond the bed height of 30 cm, a maximum 30-cm layer of coal AC may be considered as practical for DON removal in bioretention systems. Assuming actual stormwater DON = 1.0 mg N/L and 100-cm typical annual rainfall depth, a 30-cm layer

of coal-AC with superficial velocity of 61 cm/h can last for ($\frac{7.4\ m}{1\ m/yr}$ =) 7.4 years if the breakthrough depth is applied and ($\frac{52.1\ m}{1\ m/yr}$ =) 52.1 years using the exhaustion depth.

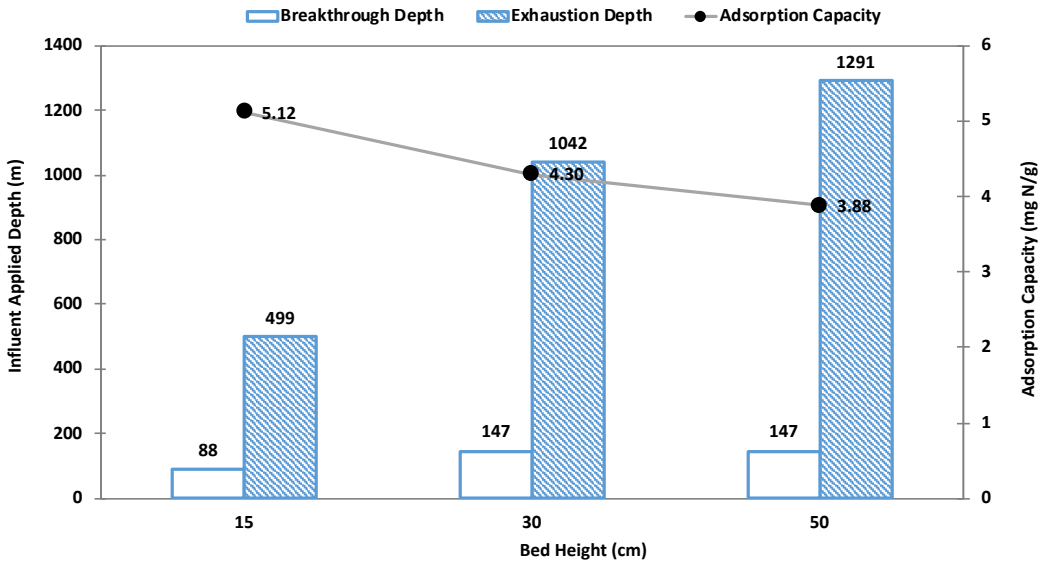


Figure 3-3. The exhaustion/breakthrough depths and column adsorption capacities for three media bed heights of 15, 30, and 50 cm

Column adsorption kinetics

Adsorption of the selected organic nitrogenous compounds on 75 g of the media mixture (22.5 g coal AC + 52.5 g sand) at different superficial velocities at 1 mg N/L influent DON is presented in Figure 3-4. For all the organic nitrogenous compounds, except for pyrrole, DON adsorption decreased as the superficial velocity increased. This trend is attributed to decreased contact time between the DON solution and the column media.

For a superficial velocity > 61 cm/h (contact time < 27 min), coal AC capability for adsorption of urea, glutamic acid, serine, and AHA varied little and diminished such that their removal efficiencies fell to less than 16%. The variation of effluent

concentration for NAG, lysine, and leucine columns was minimum beyond superficial velocity > 125 cm/h (contact time < 7 min) and their removal efficiency stayed in a range of 26-37%. However, all seven organic nitrogenous compounds had much better removal efficiencies (54-83%) at the lowest tested superficial velocity (7 cm/h) and highest contact time (134 min). On the other hand, pyrrole, a strongly adsorbable compound, was minimally affected by increased superficial velocity (reduced contact time) such that pyrrole removal efficiency stayed > 91% for all tested velocities.

Based on the results from the column adsorption kinetics study, improved DON removal efficiency was observed at low superficial velocity where the contact time between DON and the column media was the highest. To meet high-flow media conditions for efficient stormwater management, however, the superficial velocity must be increased, which may adversely decrease removal efficiency for some compounds such that DON removal efficiencies fall to less than 16%. If actual stormwater behaves similar to pyrrole, the superficial velocity can be increased up to 500 cm/h (2-min contact time) and meet high-flow media conditions. This value is about one hundred times of the maximum recommended infiltration rate for conventional bioretention systems; 1.3-5.1 cm/h; 0.5-2.0 in/h (Davis et al., 2009). For other tested organic nitrogenous compounds, the superficial velocity must be < 18 cm/h or contact time > 49 min, at which an average removal efficiency can be obtained (36-63%).

The results of column adsorption kinetics and continuous column adsorption experiments were in general agreement; the compounds with high removal efficiency in the kinetics study (> 31% removal efficiency at superficial velocity 300 mL/h)

including pyrrole, leucine, and lysine had greater exhaustion depth as well. However, NAG showed lower exhaustion depth despite > 31% removal efficiency in the kinetics study, which could be because of the column clogging, as explained earlier.

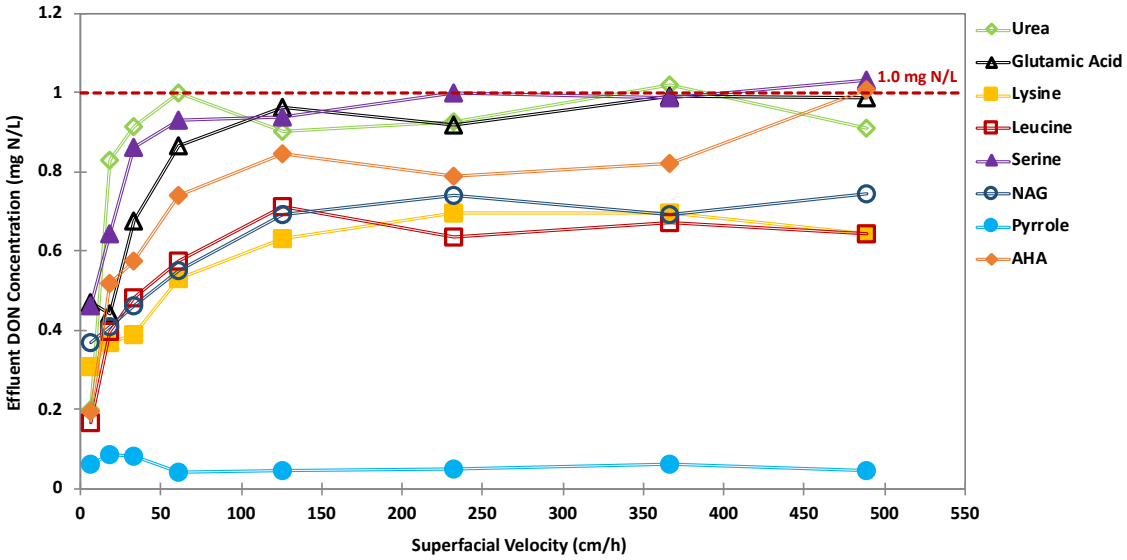


Figure 3-4. Column adsorption of the selected organic nitrogenous compounds on the media mixture of coal AC + quartz sand at various superficial velocities; Media bed height = 15 cm; Background electrolyte = 0.01M NaCl; Temperature = 22 ± 2°C; Influent DON concentration = 1 mg N/L

Recommendations for bioretention design to remove stormwater DON

Compared to batch adsorption study, column adsorption experiments provide more practical information about designing bioretention to remove stormwater DON. If actual stormwater DON behaves similar to pyrrole, a 30-cm layer of coal AC + quartz sand (70:30 by mass) or coal AC-only is recommended for stormwater DON removal, because media bed height greater than 30 cm did not show any appreciable improvement for pyrrole exhaustion depth. Also, the design infiltration flowrate for bioretention can be increased up to 500 cm/h because pyrrole adsorption was almost insensitive to flowrate increase. As estimated earlier, a 30-cm layer of coal AC + quartz

sand (70:30 by mass) with superficial velocity 61 cm/h can last for 7.4 years if the breakthrough depth is applied and 52.1 years if the exhaustion depth.

If actual stormwater DON does not behave similarly to pyrrole, another strategy such as biotransformation should be considered for removal of less adsorbable organic nitrogenous compounds; unintended ammonification in the current study suggests a possible approach for biological removal of stormwater DON, which will be discussed in Chapter 4.

Conclusions

In the current continuous column adsorption study, among eight different organic nitrogenous compounds with different physicochemical properties, only pyrrole was appreciably adsorbed by a media mixture of coal AC + quartz sand. The breakthrough and exhaustion depths for pyrrole were 88 and 499 m (equivalent to 4.4 and 25.0 m simulated rainfall depth), respectively, at a fixed superficial velocity of 61 cm/h and fixed influent DON concentration of 1 mg N/L. The breakthrough depth for other organic nitrogenous compounds was less than 15 m and their exhaustion depths lied between 44 and 191 m. Additional tests on the column adsorption of pyrrole on coal AC + quartz sand revealed that pyrrole adsorption was nearly insensitive to flowrate increase, such that pyrrole removal efficiency stayed > 91% for all the tested superficial velocities (7 to 489 cm/h). Also, it was found that media bed height greater than 30 cm did not appreciably improve pyrrole exhaustion depth. The exhaustion depths for 15-, 30- and 50-cm bed heights were 499, 1042, and 1291 m (equivalent to 25.0, 52.1, and 64.6 m simulated rainfall depth), respectively. According to these results, adsorption processes can be relied on for removing any part of actual stormwater DON with

adsorption behavior similar to pyrrole. However, to remove weakly-adsorbable stormwater DON, adsorption is possibly inadequate and other treatment measures should be considered. Unintended DON ammonification occurred despite prevention measures in this study. The DON ammonification suggests an alternative approach for removing forms of stormwater DON which is not adequately adsorbed by coal AC.

Chapter 4: Removal of Stormwater Dissolved Organic Nitrogen through Biotransformation

Abstract

Bioretention systems are stormwater control measures designed to reduce the impact of stormwater flows and quality. They are, however, not effectively designed to remove dissolved organic nitrogen (DON). This study investigated the feasibility of biotransformation, specially ammonification, in bioretention systems targeting stormwater DON removal. Biotransformation study of five organic nitrogenous compounds (urea, leucine, NAG, pyrrole, and humic acid) with different adsorbability on coal activated carbon (AC) and bioavailability showed that adsorption is a greater controlling factor for ammonification than is bioavailability. Comparing simultaneous adsorption and biotransformation of these five compounds also showed three apparent benefits: enhancement of the ammonification rate, ammonification of the bio-recalcitrant organic nitrogenous compounds, e.g. pyrrole, and bioregeneration of the adsorbent (coal AC). Low temperature (4°C) did not impact ammonification of leucine at a velocity of 34 cm/h, but negatively affected it at 61 cm/h. Also, coal AC, charcoal, and quartz sand were examined as media, and it was found that coal AC had the best performance for simultaneous adsorption and biotransformation of organic nitrogenous compounds. Although coal AC and charcoal are both porous materials, apparently adsorption properties of coal AC made it a better material for biofilm formation and DON ammonification. By testing three bed media heights (15, 30, and 50 cm), it was observed that bed media height > 30 cm would not appreciably increase ammonification. According to the results, ammonification might be considered as a possible reliable mechanism for stormwater DON removal at low temperatures > 4°C. Under intermittent wetting/draining conditions, the effluent DON was less than 0.1 mg N/L, indicating that DON was successfully removed through simultaneous adsorption/ammonification processes, although generated ammonium in the effluent must be properly addressed.

Keywords: Bioretention, Rain Garden, Stormwater, Runoff, Organic Nitrogen, Ammonification, Biotransformation

Introduction

Conveyance of nitrogen and phosphorus by stormwater runoff from land surfaces to water bodies can accelerate eutrophication (U.S. EPA, 1996, 1999; Stumm and Morgan, 2013). Bioretention is one of the most commonly used stormwater control measures (SCMs) to eliminate pollutants and nutrients transferred by stormwater to local waterbodies (Davis, 2007; Davis et al., 2009; Roy-Poirier et al., 2010; Hunt et al., 2012). Bioretention employs a set of abiotic (e.g., adsorption and filtration) and biotic (e.g., biological degradation and plant uptake) mechanisms to remove particulate and dissolved nutrients, organic compounds, and toxic metals (LeFevre et al., 2015). Removal of stormwater dissolved nitrogen is challenging because dissolved nitrogen, especially nitrite and nitrate, is not appreciably adsorbed onto bioretention media (Davis et al., 2006; Clark and Pitt, 2012).

In the soil environment, transformations among the nitrogen forms occur through biochemical reactions mediated by microorganisms (Robertson and Groffman, 2015); similar biochemical reactions can be assumed to exist in bioretention. According to Rittmann and McCarty (2001), First, dissolved organic nitrogen (DON) is converted to ammonium through biochemical ammonification (Equation 4-1). Then, the ammonium is transformed first to nitrite and then to nitrate; this nitrification process occurs under aerobic conditions (Equations 4-2 and 4-3). The final step is denitrification through which nitrate is converted to nitrogen gas under anoxic conditions with an electron donor, typically as organic chemical (Equation 4-4).

$$\mathrm{DON} + 4\mathrm{H_2O} \rightarrow \mathrm{NH_4^+} + 4\mathrm{OH^-} \quad (4\text{-}1)$$

$$\mathrm{NH_4^+} + \frac{3}{2}\mathrm{O_2} \rightarrow \mathrm{NO_2^-} + 2\mathrm{H^+} + \mathrm{H_2O} \quad (4\text{-}2)$$

$$\mathrm{NO_2^-} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{NO_3^-} \quad (4\text{-}3)$$

$$\frac{5}{4}\mathrm{CH_2O} + \mathrm{NO_3^-} \rightarrow \frac{5}{4}\mathrm{CO_2} + \frac{1}{2}\mathrm{N_2} + \frac{3}{4}\mathrm{H_2O} + \mathrm{OH^-} \quad (4\text{-}4)$$

The application of these biochemical processes has been investigated in control of stormwater dissolved nitrogen. Laboratory and field studies have been conducted on removal of stormwater nitrate/nitrite by creating a denitrification zone in bioretention cells. This internal water storage (IWS) zone is designed to stay saturated between storm events such that anoxic conditions could be developed to promote denitrification (Kim et al., 2003; Hsieh et al., 2007; Ergas et al., 2010; Peterson et al., 2015; Igielski et al., 2019). Residence time, media type, temperature, and organic carbon content were shown to be effective factors controlling the extent of denitrification in bioretention systems (LeFevre et al., 2015). Ammonium has been found to be removed from synthetic stormwater through adsorption during stormwater dosing and through nitrification during subsequent dry periods; a sandy coarse soil layer over fine soil layer with a 10% slit/clay content showed the best performance for ammonium removal (Cho et al., 2009).

In addition to stormwater inorganic nitrogen, biological removal can be considered for stormwater DON removal. Based on laboratory studies, a large fraction of rainwater dissolved organic nitrogen is biologically available (45-70%, Chen et al., 2011). Karanfil (2006) found that biological treatment removed non-adsorbable organic

matter in drinking water and the efficiency of adsorption improved with increased levels of biological activity. It was also revealed that biodegradation processes tend to remove hydrophilic substances, leaving behind more hydrophobic organic matter, which happens to be more adsorbable. As discussed in Chapter 3, unintended ammonification was also detected during adsorption columns studies despite the preventative measures taken. The highest effluent ammonium concentration was measured for leucine as 0.69 mg N/L at the end of experiment. As a result, biochemical processes, specifically ammonification, can be examined for removal of stormwater DON removal, specially poorly-adsorbable fractions, as it has been done for stormwater inorganic nitrogen (nitrate and ammonium) removal.

Specific research on biological removal of stormwater DON has not been identified. However, biofilters have been studied at biological treatment of drinking water (Moll et al., 1998; Fonseca et al., 2001; Yapsakli and Çeçen, 2010; Velten et al., 2011; Liao et al., 2013; McKie et al., 2016; Terry and Summers, 2018), containing organic compounds with similar concentrations to stormwater. In drinking water biofiltration, the bed material provides required surface area for microbial colonization which may eventually establish an active biofilm (Huang and Chen, 2004; Kasuga et al., 2007; Velten et al., 2011). Slow sand filters represent a well-established form of biofilters used in potable water treatment. Slow sand filters facilitate formation of a gelatinous layer or biofilm on the sand layer; the biofilm can promote removal of microbial contaminants as well as total organic carbon (Edzwald, 2011; Yildiz, 2012; Brandt, 2017). While microbial colonization may promote biodegradation of organic compounds, it may also have adverse effects such as bed media clogging and dead

zones formation (Emelko et al., 2006; Laurent et al., 2003; Putz et al., 2005). For instance, slow sand filters slowly lose their performance as the biofilm thickens and thereby reduces the rate of flow through the filter (Brikké and Bredero, 2003). The extent of biofilm formation and biodegradation depends on different factors such as type of substrates, type of bed materials, contact time, temperature, pH and background electrolyte among others (Moll et al., 1998; Urfer and Huck, 2001; Emelko et al., 2006; Zhu et al., 2010; Velten et al., 2011). All of these factors also determine the extent of adsorption, which may positively or negatively affect the biodegradation process of organic compounds. Adsorbed compounds may be less bioavailable because they are less likely to be present in aqueous phase (Gordon and Millero, 1985; Ogram et al., 1985; Robinson et al., 1990; Smith et al., 1992; Knaebel et al., 1996; Nam et al., 1998). On the other hand, attached microbes may benefit from slow biodegradation of adsorbed compounds because of longer detention time (Griffith and Fletcher, 1991; Marchesi et al., 1997; Carlson and Silverstein, 1998).

Different bed materials have different potential for microbial growth. While sand is the dominant bed material used in slow sand filters, granular activated carbon has been another popular material employed in drinking water treatment. Granular activated carbon contains numerous micro- and macro-pores which provide larger specific surface area compared to quartz sand, the convectional material used in bioretention media, whose surface is non-porous (Suárez-Ruiz and Crelling, 2008; Yapsakli and Çeçen, 2010; Singh, 2015). The larger specific surface area provides more accessible area for microbial growth. Moreover, the amorphous structure of granular activated carbon can protect attached bacteria from shear forces, which is one the of

obstacles in biofilm formation (Urfer et al., 1997; Liu et al., 2001). Consequently, activated carbon has been extensively studied and used as the biofiltration material, so-called biological activated carbon (BAC), for biological removal of organic compounds in drinking water treatment. Consequently, granular activated carbon can be considered for further study on biological removal of stormwater DON in bioretention systems.

In practice, bioretention systems serve intermittent storm events, causing frequent media draining/wetting, which dramatically affects biochemical reactions, including nutrient release and microbial growth. While adsorption mainly occurs during the wetting period in bioretention systems, biological removal of organic pollutants mainly takes place during longer drying periods (LeFevre et al., 2015; Subramaniam et al., 2016). For example, nitrification and denitrification in bioretention systems was found to occur primarily during drying periods rather than wetting periods (Cho et al., 2009; Subramaniam et al., 2016). Accordingly, to have a comprehensive view about the practicability of ammonification in stormwater DON removal, effect of wetting and draining regimes in bioretention systems should be investigated.

The current study focuses on the effectiveness of ammonification for stormwater DON removal in adsorption/biotransformation columns. The study objectives are:

- Investigate how various types of organic nitrogenous compounds and their adsorbability on bioretention bed material affect stormwater DON ammonification;
- Determine if less expensive material, rather than activated carbon, can be used as an acceptable bed media to promote stormwater DON ammonification in bioretention systems;

- Find a practical contact time between organic nitrogenous compounds and biofilm by changing superficial velocity and bed media height in order to enhance stormwater DON ammonification in bioretention systems;
- Investigate if stormwater DON ammonification in bioretention systems can be relied on for stormwater DON removal in a cold weather condition;
- Study effects of a wetting/draining regime on stormwater DON ammonification in bioretention systems.

Materials and Methods

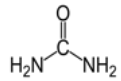
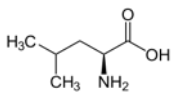
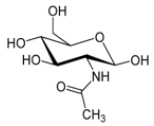
Selection of organic nitrogenous compounds

Many different organic nitrogenous compounds exist in the environment; from simpler compounds such as urea to more complex compounds such as amino sugars, amino acids, heterocyclic nitrogenous compounds. Five organic nitrogenous compounds were selected for this study, based on their adsorbability and bioavailability properties (Table 4-1). The adsorption capacity of these compounds on Filtrasorb® 200 coal activated carbon (coal AC) and their other physical/chemical characteristics are shown in Table 4-1.

Based on the adsorption capacities on coal AC, pyrrole and N-acetyl-D-glucosamine (NAG) were considered as high adsorbability compounds, while leucine and Aldrich humic acid (AHA) were classified as medium adsorbability; urea was considered as low adsorbing with < 0.01 mg N/g on coal AC (Mohtadi et al., 2017). Studies have shown NAG, leucine and urea are bioavailable, while pyrrole and AHA are refractory organic compounds for biodegradation (Subbaramaiah et al., 2013; Singh

et al., 2015; Li et al., 2016; Hiwarkar, Singh et al., 2017; Fan et al., 2018). These five compounds were examined to see how their different adsorbability and bioavailability properties might affect biotransformation of synthetic stormwater DON. To examine effects of bed material type, temperature, bed height, and frequent wetting/draining regimes only leucine was used.

Table 4-1. Selected organic nitrogenous compounds used for stormwater DON biotransformation

Organic Nitrogenous compound		**Chemical structure** [1]	**Molar mass (g/mole)**[1]	**pKa$_1$** [1]	**pKa$_2$** [1]	**Log K$_{ow}$** [1]	**Solubility at 25°C (mg/mL)**[1]	**Adsorbability on coal AC (Adsorption capacity, mg N/g at C$_e$ = 1.0 mg N/L)**[2]	**Bioavailability**[3]	**Manufacturer**
Urea	-		60.06	0.10	-	-2.11	545	Low (< 0.01)	Bioavailable	Fisher Scientific, Pittsburgh, Pennsylvania
Amino acid	L-Leucine		131.17	2.36	9.63	-1.52	21.5	Medium (0.10)	Bioavailable	Acros Organics, Geel, Belgium
Amino sugar	N-acetyl-D-glucosamine (NAG)		221.21	11.56	-	-2.10	148	High (0.80)	Bioavailable	Alfa Aesar, Ward Hill, Massachusetts
Humic acid	Aldrich humic acid (AHA)	-	-	1.6 [4]	-	-	-	Medium (0.05)	Bio-recalcitrant	Sigma Aldrich, St. Louis, Missouri
Heterocyclic nitrogen	Pyrrole		67.09	17.5	-	0.75	45	High[5] (0.40)	Bio-recalcitrant	Acros Organics, Geel, Belgium

[1] NIH (2019)

[2] Mohtadi et al. (2017)

[3] Subbaramaiah et al. (2013); Singh et al. (2015); Li et al. (2016); Hiwarkar, Singh et al. (2017); Fan et al. (2018)

[4] pH_{pzc} (Zhang and Bai, 2003)

[5] at C_e = 0.02 mg N/L

Preparation and characterization of bed materials

Coal AC was the primary bed material used for biofilm development. To compare coal AC with less expensive materials, charcoal and quartz sand were also examined as bed materials to enhance biofilm formation for ammonifying synthetic stormwater DON. These materials were used unwashed to promote biofilm formation. The characteristics of coal AC, quartz sand, and their mixture are shown in Table 4-2.

The bulk and particle densities and porosities were determined according to ASTM (2009) D7263-09. The specific area of coal AC were measured based on N_2-isotherms using the BET model by using ASAP 2020 surface area and porosimetry analyzer, made by Micromeritics Instrument, Norcross, Georgia. All samples were degassed at 150°C prior to N_2 adsorption measurements. The total pore volume and average pore size were also determined for coal AC by using ASAP 2020 analyzer.

Table 4-2. Characterization of the bed materials used for stormwater DON biotransformation

Media	Product/ Cat number	Particle					Media		Manufacturer
		Effective size (mm)	Specific surface area (m^2/g)	Total pore volume (mL/g)	Average pore size (Å)	Particle density (g/L)	Bulk density (g/L)	porosity (%)	
Coal AC	Filtrasorb® 200	0.55-0.75	798	0.198	53.3	1503 ± 19	498 ± 19	57 ± 2	Calgon Carbon, Pittsburgh, Pennsylvania
Quartz sand	Ottawa silica C-778 (20-30 grade)	0.5-1.0	-	-	-	2533 ± 58	1603 ± 4	37 ± 1	US Silica, Frederick, Maryland
Charcoal	Hardwood lump	1.7-2.0	-	-	-	670 ± 25	273 ± 17	59 ± 1	Royal Oak, Bradleyville, Missouri

Column setup and DON biotransformation

The details of experiments performed for DON biotransformation are listed in Table 4-3. According to the batch adsorption study by Mohtadi et al., (2017), the influent DON concentration and ionic strength were set at 1 mg N/L and 0.01 M NaCl, respectively. The experiments were conducted in glass cylindrical columns having 2.5 cm inner diameter and different heights (15, 30, and 50 cm), made by Kimble-Chase (Rockwood, Tennessee). The 15-, 30- and 50-cm columns were packed using 43, 89 and 145 g of coal AC. Also, 61 g of quartz sand and 23 g of charcoal were used to pack 15-cm columns for studying effect of bed material type on DON biotransformation. To study the performance of ammonification in cold weather conditions, a 15-cm column packed with coal AC was set up in a refrigerator keeping the temperature at 4°C. The influent solution container was also placed inside the refrigerator, but the peristaltic pump was installed outside of the refrigerator. For the wetting/draining experiment, the columns were kept running for 24 hours (twice a week) and kept off in between. Because of very low C:N ratio of urea, 0.43, and undesirable ammonification results, 0.1367 g of sodium acetate (anhydrous) was added to each 10 L of the urea influent solution (after day 79) to increase organic carbon concentration from 0.43 to 4 mg C/L and promote ammonification. Sodium acetate (anhydrous) was supplied from Fisher Scientific, Pittsburgh, Pennsylvania.

It must be noted that the experimental conditions, e.g. temperature, media bed height and volume, and flowrate, for biotransformation study of urea, leucine, NAG, AHA, and pyrrole at velocity of 61 cm/h are very similar to adsorption study of these compounds presented in Chapter 3; however, their adsorption media beds are different:

the current biotransformation study employed a mixture of coal AC and quartz sand (70:30 by mass) and the Chapter 3 adsorption study used only coal AC as the bed media.

Table 4-3. List of experiments for stormwater DON biotransformation

Experiment	Compound	Continuous/ Intermittent	Temperature (°C)	Bed material	Height (cm)	Flowrate (mL/h)	Superficial velocity (cm/h)	EBCT (min)	CT (min)
Effect of type of organic nitrogenous compound	Urea	Continuous	22 ± 2	Coal AC	15	165 and 300	34 and 61	27 and 15	15 and 8.4
	Leucine								
	NAG								
	AHA								
	Pyrrole								
Effect of temperature	Leucine		4	Coal AC	15	165 and 300	34 and 61	27 and 15	15 and 8.4
			22 ± 2						
Effect of bed material type	Leucine		22 ± 2	Coal AC	15	165	34	27	15
				Charcoal					16
				Quartz sand					10
Effect of bed height (contact time)	Leucine		22 ± 2	Coal AC	15	165 and 300	34 and 61	27 and 15	15 and 8.4
					30			54 and 29	31 and 17
					50			89 and 49	51 and 28
Wetting/draining regime	Leucine	Intermittent	22 ± 2	Coal AC	15	165 and 300	34 and 61	27 and 15	15 and 8.4

Peristaltic pumps and MasterFlex® tubing by Cole-Parmer Instrument Co. (Chicago, Illinois) were used to feed the columns at the desired flowrate. To avoid channeling, the columns were designed to operate up-flow. All experiments were run at flowrates of 165 and 300 mL/h, equivalent to 34 and 61 cm/h, respectively. These flowrates are comparable to 10-40 cm/h used in slow sand filters (Fox et al., 1994). The

equivalent superficial velocity, empty-bed contact time (EBCT), and true contact time (CT) were calculated using Equations 4-5 and 4-6 as shown in Table 4-3.

$$\mathrm{EBCT} = \frac{\mathrm{L}}{\mathrm{v_s}} \tag{4-5}$$

$$\mathrm{CT} = \frac{\mathrm{L}}{\mathrm{v_p}} = \frac{\mathrm{L}}{\mathrm{v_s}/\emptyset} = \frac{\mathrm{L}}{\mathrm{v_s}} \times \emptyset \tag{4-6}$$

where L is bed media height; $\emptyset$ is media porosity; v_p is pore velocity; and v_s is superficial velocity.

Flowrate was converted to applied depth (cumulative influent volume per unit area treated) by

$$\text{applied depth} = \frac{\mathrm{Q\,t}}{\mathrm{A}} \tag{4-7}$$

where Q is volumetric flowrate (mL/h); A is cross-sectional surface area of column (cm^2); and t is column adsorption duration (d).

Analytical methods

A summary of analytical methods used in this study is shown in Table 4-4. The synthetic stormwater samples did not contain any particulate matter. It is expected that any particulate matter would be filtered from the stormwater in upper media layers. Each sample was tested for total nitrogen (TN), ammonium nitrogen (NH_4^+-N), and nitrate nitrogen (NO_3^--N). Nitrite nitrogen (NO_2^--N) was measured in random samples; because nitrite was less than the detection limit of 0.01 mg N/L, it was considered as negligible in the calculations. DON was calculated by subtracting NO_3^--N and NH_4^+-N

from TN. The analytical methods used in this study are presented in Table 4-4. All nitrogen forms are reported as mg N/L.

Table 4-4. Summary of analytical methods for water quality analysis

Parameters	Analytical method	Detection limit
pH	Mettler Toledo MA 235	-
Dissolved oxygen (DO)	Hach sensION 6 dissolved oxygen meter	-
Total nitrogen (TN)	Shimadzu TOC/TN analyzer (TOC-L + TNM-L series)	0.05 mg N/L
Ammonium nitrogen (NH_4^+-N)	4500NH_3 (F)[1]	0.02 mg N/L
Nitrate nitrogen (NO_3^--N)	4500NO^-_3 (C)[1]	0.05 mg N/L
Nitrite nitrogen (NO_2^--N)	4500NO^-_2 (B)[1]	0.01 mg N/L
Dissolved organic nitrogen (DON)	= TDN – ([NH_4^+-N] + [NO_3^--N])	N/A

[1] APHA (2005)

The samples were collected 2-3 times a week for all columns. The collected samples were stored in centrifuge tubes and kept cold at 4°C. All laboratory devices and analytical procedures were calibrated before use. Six standards were used for every analytical procedure and R-squared for the standard curves was not less than 0.95. Some samples were randomly reanalyzed to ensure variation of two measurements did not exceed 10%; otherwise, all samples were reanalyzed for that run. All glassware used in water quality analysis were acid-washed before use.

Results and Discussion

Biotransformation of the selected organic nitrogenous compounds

Figure 4-1 shows effluent DO, TN, DON and ammonium concentrations as a function of influent applied depth for biotransformation and adsorption of urea, leucine, NAG, AHA, and pyrrole on coal AC at two velocities of 34 and 61 cm/h. The effluent

ammonium concentration was assumed to be steady when its variation was less than 5%. Accordingly, the final concentration was averaged for the last 3-5 effluent samples assuming steady-state concentrations. A summary of the results for these five examined compounds is presented in Table 4-5. Because the influent stormwater solution is synthetic and free of suspended solids, TN is equal to TDN and DON for the influent water and equal to TDN for the effluent water. Nitrate results were added only to the NAG figure (Figure 4-1) because both nitrate and nitrite were negligible (less than the detection limit of 0.05 and 0.01 mg N/L, respectively) for the four other compounds. Although this study focuses on DON ammonification, nitrate/nitrite concentrations were also monitored to investigate any possible nitrification activity, as a part of the possible biological mechanisms for stormwater nitrogen transformation.

According to Figure 4-1-a, in terms of TN, the urea column exhausted only after an applied depth of 32 m. Exhaustion is defined as when the effluent concentration increases up to 0.95 of influent concentration (Jain, 1997; Wang et al., 2007); accordingly, the exhaustion threshold in the current study is 0.95 mg N/L. Fast exhaustion indicates low adsorption capacity of urea on coal AC, which is in agreement with the batch adsorption results; the batch adsorption capacity of urea on coal AC was measured < 0.01 mg N/g at C_e = 1 mg N/L (Table 4-1 ; Mohtadi et al., 2017). Urea has been used extensively as fertilizer because of its bioavailability, but urea average ammonification was surprisingly very low (2 ± 2%) in this study before addition of an organic carbon source; accordingly, the main mechanism for DON removal in the urea column was adsorption because average DON removal efficiency was 10 ± 3%, where

the difference between DON removal efficiency and ammonification shows the level of adsorption, 8%.

Urea ammonification, a hydrolysis process mediated by microbes through production of urease enzyme, was found to be significantly correlated with the soil carbon and nitrogen content (Fisher et al., 2016). As a general rule, organic compounds with a C:N < 25:1 stimulate ammonification while those with C:N > 25:1 stimulate immobilization in soils (Paul, 2015). Also lower soil C:N was found to be associated with high nitrification rates in forests (Ross et al., 2004). While microbes become nitrogen-limited in high C:N ratio treatments, in low C:N ratio treatments, without nitrogen limitation, the microbial activity can be limited due to exhaustion of available carbon (Eiland et al., 2001; Post and Mann, 2005). Demoling et al. (2007) also reported that even soils with a C:N ratio of 28 could be carbon-limited for microbial activity. Accordingly, although the urea C:N ratio of 0.43 may promote its ammonification, low carbon content of urea (20% by mass) may limit its decomposition. As shown in Figure 4-1-a, sodium acetate was added to the influent urea solution at an applied depth of 758 m to provide an organic carbon concentration of 4 mg C/L and increase the C:N ratio from 0.43 to 3.86. By increasing the C:N ratio, signs of ammonification appeared where an effluent average ammonium concentration of 0.13 ± 0.02 mg N/L was detected. At this point, ammonification can be considered as the main mechanism for DON removal because ammonification and DON removal efficiency have the same amount (Table 4-5).

Table 4-5. Summary of the results for the selected organic nitrogenous compounds

Organic nitrogenous compound	Influent TN concentration (mg N/L)	Influent TC concentration (mg N/L)	C:N ratio	Effluent steady-state average pH		Effluent steady-state average DON concentration (mg N/L)		Effluent steady-state average ammonium concentration (mg N/L)		Average DON removal efficiency (%)		Average Ammonification (%)	
				34 cm/h	61 cm/h	34 cm/h	61 cm/h	34 cm/h	61 cm/h	34 cm/h	61 cm/h	34 cm/h	61 cm/h
Urea	1.0	0.43	0.43	5.89 ± 0.18	6.19 ± 0.16	0.90 ± 0.03	0.87 ± 0.05	0.02 ± 0.02	0.13 ± 0.02	10 ± 3	13 ± 5	2 ± 2	13 ± 2
Leucine	1.0	5.14	5.14	5.65 ± 0.35	5.44 ± 0.22	0.03 ± 0.03	0.87 ± 0.03	0.55 ± 0.01	0.26 ± 0.02	97 ± 3	13 ± 3	55 ± 1	26 ± 2
NAG	1.0	7.60	7.60	5.64 ± 0.17	-	0.78 ± 0.02	-	0.05 ± 0.02	-	22 ± 2	-	5 ± 2	-
AHA	1.0	32.8	32.8	7.06 ± 0.25	7.65 ± 0.23	0.90 ± 0.05	0.80 ± 0.04	0.09 ± 0.00	0.05 ± 0.04	10 ± 5	20 ± 4	9 ± 0	5 ± 4
Pyrrole	1.0	3.43	3.43	5.90 ± 0.25	5.46 ± 0.18	0.02 ± 0.02	0.60 ± 0.06	0.55 ± 0.04	0.05 ± 0.01	98 ± 2	40 ± 6	55 ± 4	5 ± 1

The low ammonification could be due to the lack of a developed biofilm on the coal AC. The first step in biofilm formation is adsorption and formation of a layer of organic compounds on the media surface (Baier, 1973; Fletcher, 1980; Trulear and Characklis, 1982), which might be challenging in this case because of the low adsorption capacity of coal AC for urea. Based on Figure 4-1-a, urea ammonification adversely affected the effluent DO and DON concentrations. Ammonification takes place under both aerobic and anaerobic conditions but proceeds faster in oxygen-rich environments (Stefanakis et al., 2014). Due to sufficient amount of DO in the influent, 7.29 ± 1.16 mg O_2/L, aerobic microorganisms should be responsible for DON ammonification and reduction of the effluent DO.

Another important factor that affects biotransformation processes, e.g. ammonification, is attraction/repulsion between substrate compounds and a biofilm surface. Biofilms consist of bacterial cells growing in self-produced matrix of extracellular polymeric substances (EPS) (Characklis and Marshall, 1990; Mah and O'Toole, 2001). The EPS matrix contains chemically-active sites adsorbing cations and organic molecules (Characklis and Marshall, 1990). Due to the dominance of some functional groups (e.g., carboxyl, hydroxyl, etc.) on EPS, biofilms are generally negatively-charged at neutral pH (Horan and Eccles, 1986; Morgan et al., 1990; Ding et al., 2018). Adsorption and transport of charged compounds from water into biofilm are likely to be affected by net negative surface charge of the biofilm. As a result, biosorption of negatively-charged molecules into biofilms would be inhibited due to electrostatic repulsion by the negatively-charged EPS matrix (Carlson and Silverstein, 1998). Based on the column effluent pH (Table 4-5) and pK_a (Table 4-1) for urea, the

dominant form of urea would be neutral-polar, such that negatively-charged biofilm surface should not affect the transport of urea into biofilm matrix.

Figure 4-1-b shows that, at a velocity of 34 cm/h, leucine ammonification averaged 55 ± 1% and average DON removal efficiency was 97 ± 3%; the difference between these two percentages shows the level of DON adsorption, 42%, indicating the almost equal contribution of ammonification and adsorption to DON removal. The previous batch (Mohtadi et al., 2017) and column (Chapter 3) adsorption studies also confirms the presence of leucine adsorption on coal AC. By increasing the velocity to 61 cm/h, uncertainties appeared, and effluent ammonium concentration started to decrease while DON concentration increases. At the end of 61 cm/h experiment, leucine average ammonification decreased to 26 ± 2%, average DON removal efficiency decreased to 13 ± 3%, and the TN concentration passed the exhaustion threshold of 0.95 mg N/L; these simultaneous reductions in both ammonification and adsorption may be related to decrease in contact time between leucine molecules and biofilm/adsorbent surface. DO concentration decreased as more ammonification occurred and vice versa, indicating that ammonification occurred under aerobic conditions.

At both tested velocities, effluent average pH for the leucine column was measured > 5.22 (Table 4-5), which was between pKa_1 and pKa_2 values (Table 4-1), meaning that leucine dominant form was neutral non-polar during the experiment. Adsorption and transport of a neutral non-polar compound should minimally be affected by negatively-charged biofilm surface. Leucine had the best performance for both DON removal and ammonification among the examined organic nitrogenous compounds in

the current study, possibly due to combination of bioavailability and adsorbability on coal AC (0.1 mg N/g at C_e = 1.0 mg N/L; Table 4-1; Mohtadi et al., 2017).

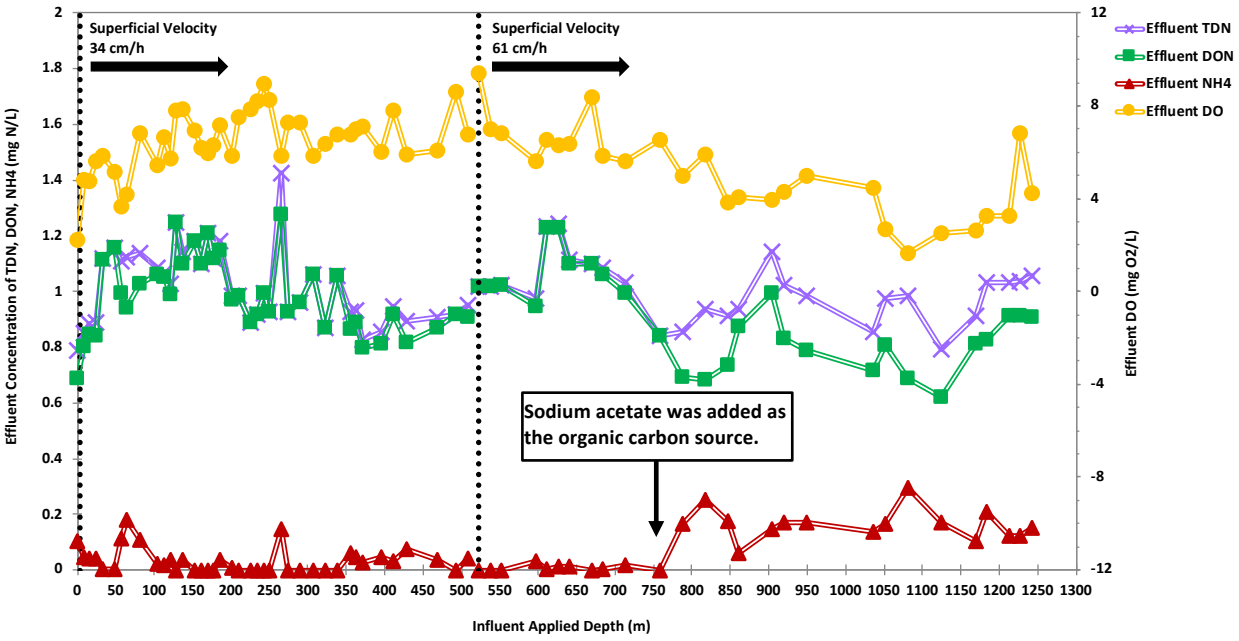
Figure 4-1-c shows that nearly 100% DON removal efficiency was observed for the NAG column, up through the applied depth of 97 m, as a result of its high adsorption on coal AC (0.80 mg N/g at C_e = 1 mg N/L; Table 4-1; Mohtadi et al., 2017). Beyond the applied depth of 97 m, the effluent DON concentration increases to 0.78 ± 0.02 mg N/L, where the column exhausted with respect to TN (> 0.95 mg N/L). NAG was the only examined compound that showed nitrification in its experimental column such that the maximum nitrate concentration of 0.47 mg N/L was observed at applied depth of 24 m. The highest ammonium concentration of 0.96 mg N/L was also detected at applied depth of 48 m. However, both ammonium and nitrate concentrations dropped to less than 0.07 mg N/L at the end of this experiment despite the bioavailability of NAG, possibly caused by column clogging. The column clogged due to formation of a clear thin film on the activated carbon granules; the same problem was observed during the NAG column adsorption experiments presented in Chapter 3. The clear film was probably hydrogel because NAG is one of the major components that form hydrogel in nature, e.g., chitosan, and has been used to make synthetic hydrogel (Park et al., 2002; Qiu et al., 2011). This film possibly blocked coal AC surface exposure to NAG molecules. Because the column clogged, the velocity of 61 cm/h could not be tested.

Figure 4-1-d shows that pyrrole was first only adsorbed on coal AC and no evidence of ammonification was seen until an applied depth of 355 m, where ammonium started to be detected in the effluent and effluent DO concentration also started to decrease, an indicator of aerobic ammonification. At the end of the 34 cm/h phase, the effluent

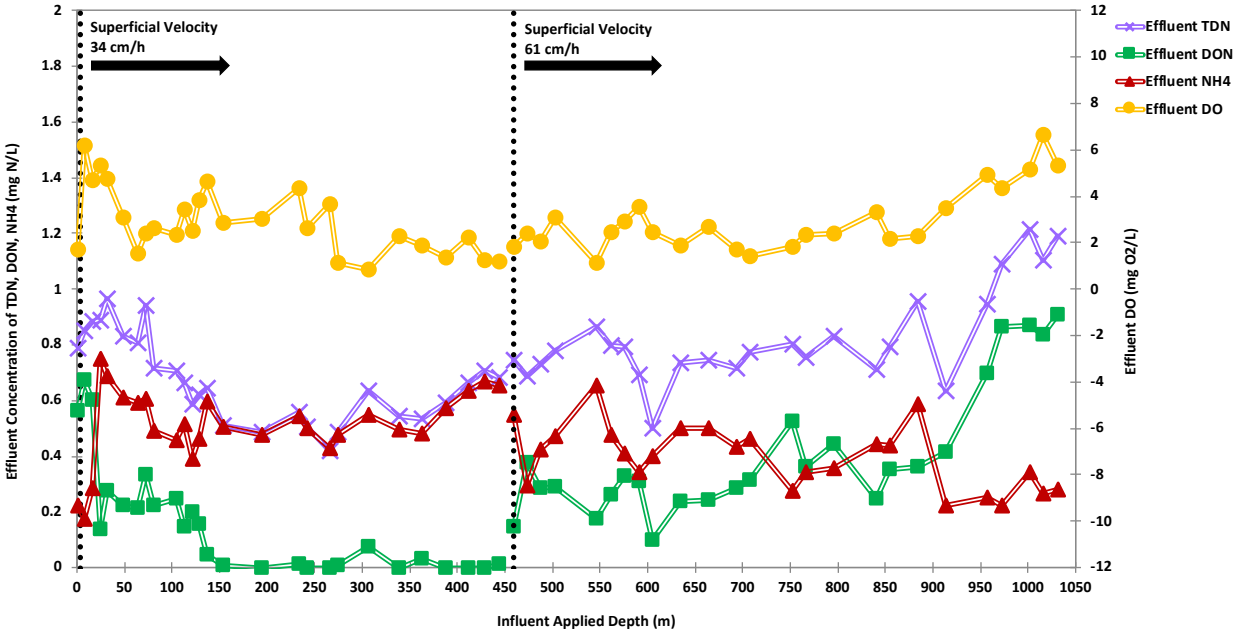
average ammonium concentration was 0.55 ± 0.04 mg N/L and average DON concentration was 0.02 ± 0.02 mg N/L (DON removal efficiency = 98 ± 2%); this means approximately 43% of DON removal was due to the adsorption process almost equal to the share of ammonification in DON removal. This level of adsorption on coal AC was expected for pyrrole as previous adsorption studies revealed the high adsorption capacity of coal AC for pyrrole; the batch adsorption capacity was calculated as 0.4 mg N/g at C_e = 0.02 mg N/L (Table 4-1; Mohtadi et al., 2017) and column adsorption capacity was estimated as 4.62 mg N/g (Chapter 3). Once velocity increased to 61 cm/h, DON removal and ammonification showed uncertainties and continuously decreased such that effluent average ammonium concentration dropped to 0.05 ± 0.01 mg N/L, effluent DO concentration increased, and average DON concentration reached 0.60 ± 0.06 mg N/L (DON removal efficiency = 40 ± 6%). Like the leucine column, the concurrent decrease in both DON removal efficiency and ammonification was possibly rooted in reduced contact time between pyrrole and biofilm/adsorbent surface as result of increase in the velocity.

Heterocyclic aromatic compounds (e.g., pyrrole) are resistant to biodegradation because of their rigid chemical structure in water (Subbaramaiah et al., 2013; Singh et al., 2015; Li et al., 2016). Additionally, adsorbed compounds may become less accessible to microorganisms because they are less likely to be present in the aqueous phase (Ogram et al., 1985; Robinson et al., 1990; Smith et al., 1992; Knaebel et al., 1996; Nam et al., 1998). Accordingly, it had been hypothesized that the high adsorption capacity of coal AC for pyrrole and its bio-recalcitrant nature would adversely affect pyrrole ammonification. However, ammonification was detected after a depth of 355

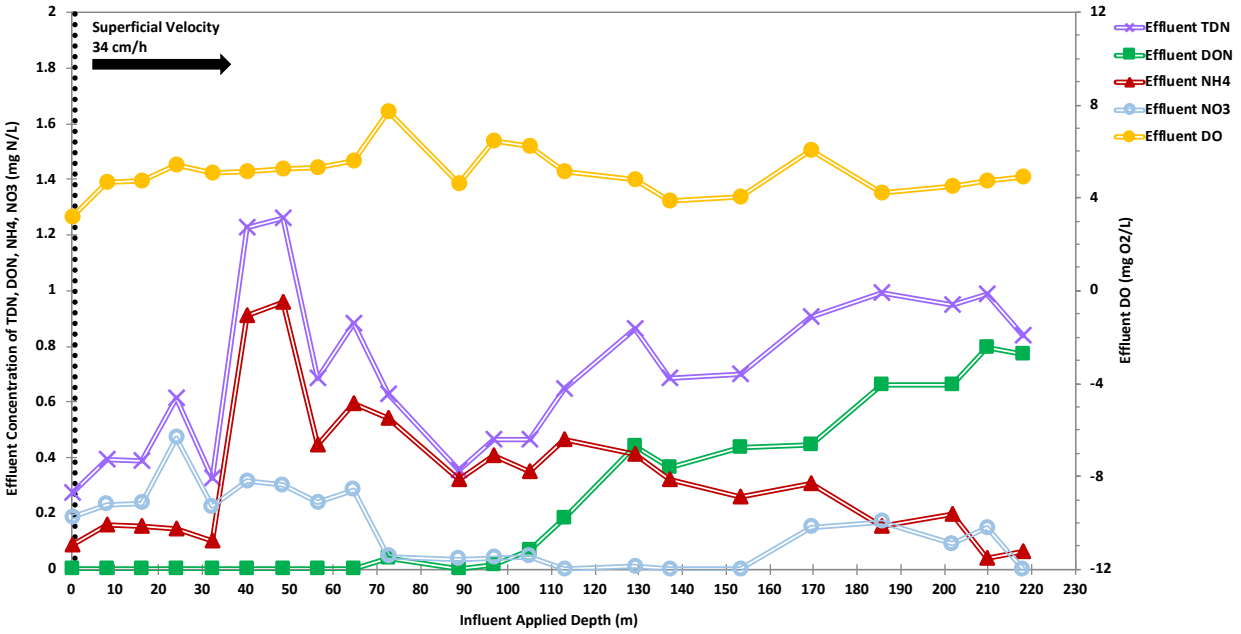
m, possibly because adsorption provided a long retention time for pyrrole, which gave the ammonifiers able to degrade pyrrole enough time for colonization. Similarly, Carlson and Silverstein (1998) suggested that recalcitrant natural organic matter might be removed by adsorption onto biofilms first, then microbes slowly degrade them because of longer detention time within the biofilm. It must be noted that the negatively-charged biofilm surface have possibly had a limited effect on transfer of pyrrole into the biofilm matrix, because pyrrole was dominantly available in neutral non-polar form during the experiment; the pyrrole effluent pH at both velocities (Table 4-5) was much less than $pK_a = 17.5$ (Table 4-1).



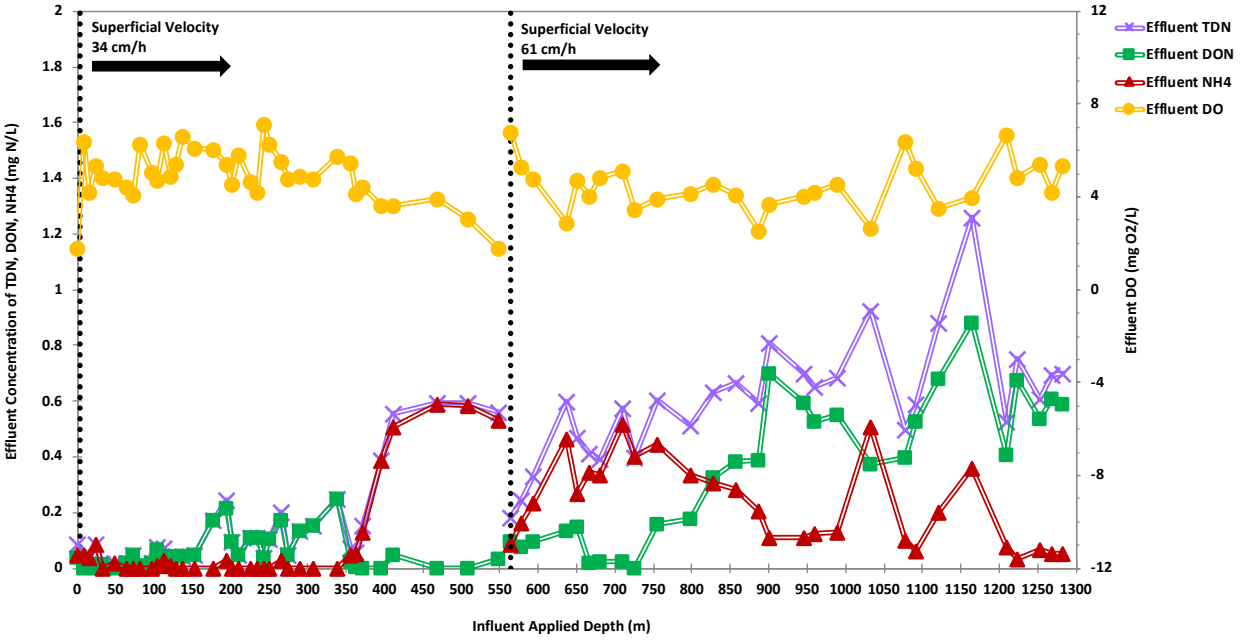
(a) Urea



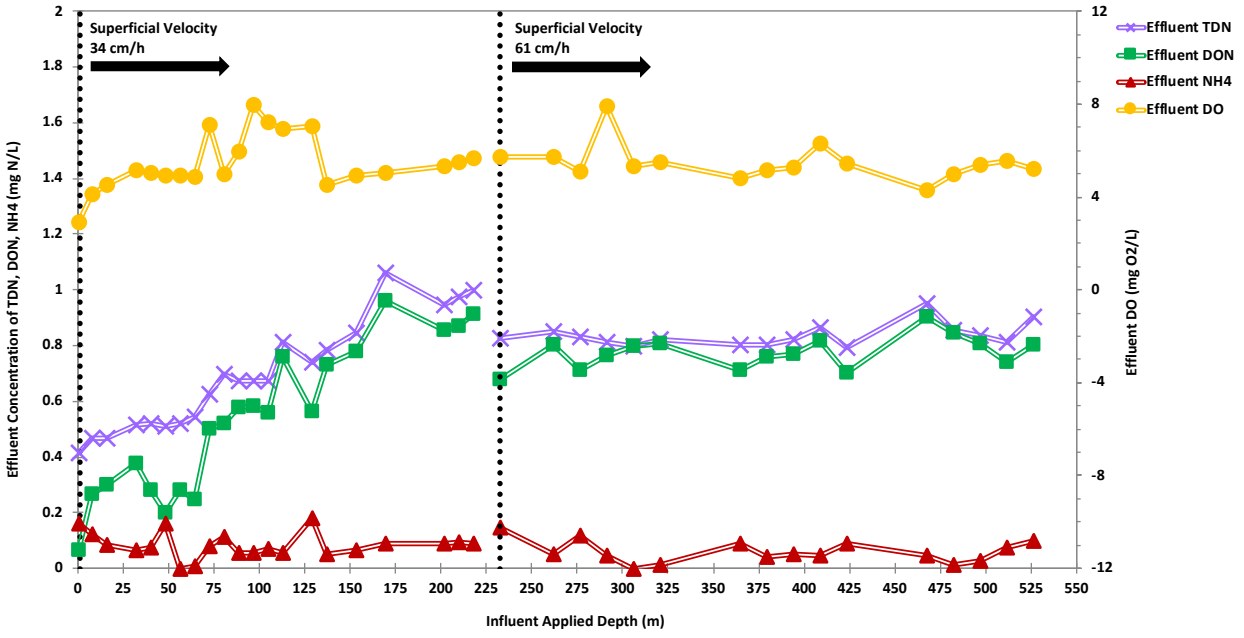
(b) Leucine



(c) NAG



(d) Pyrrole



(e) AHA

Figure 4-1. Biotransformation of the selected organic nitrogenous compounds on coal AC at two superficial velocities (34 and 61 cm/h). Bed height = 15 cm; Bed mass = 43 g; Influent concentration = 1 ± 0.1 mg N/L; Background electrolyte = 0.01M NaCl; Temperature = 22 ± 2°C.

According to Figure 4-1-e, average DON removal efficiency for AHA was 10 ± 5% and 20 ± 4% at velocities of 34 and 61 cm/h, respectively. The average ammonification was also 9 ± 0% and 5 ± 4% for both velocities of 34 and 61 cm/h, respectively. Comparing these results shows that DON adsorption contributes only 1-15% to DON removal. Low adsorption level of AHA on coal AC was also observed in the previous batch and column adsorption studies, such that the batch adsorption capacity for AHA was reported 0.05 mg N/g at C_e = 0.1 mg N/L by Mohtadi et al., 2017 (Table 4-1). Effluent DO concentration did not change significantly, illustrating that aerobic ammonification was limited and DO consumption by ammonifiers was low, which is in agreement with the low level of ammonification. AHA has also been found to be bio-recalcitrant (Carlson and Silverstein, 1998). Low adsorption capacity and low bioavailability together would make AHA a challenging compound for removal.

The hydrodynamic radius for different types of humic acid has been reported to lie in the range of 2.42-12.8 nm (Österberg et al., 1993; Kawahigashi et al., 2005; Kawahigashi et al., 2011), while the coal AC average pore size was measured at 5.33 nm. Accordingly, it was likely that a part of the pore volume of the activated carbon was unavailable to large humic acid molecules, also reported by Daifullah et al., (2004) and Lin et al. (2012), resulting in low adsorption capacity of AHA on coal AC. Similar to urea, low adsorption of organic compounds may lead to lack of the prerequisite initial organic layer on coal AC required for development of biofilm, which can reduce ammonification. Additionally, the C:N ratio for AHA is 32.8, more than the maximum desirable value of 25 discussed earlier, which can be another limiting factor for ammonification of AHA.

Another factor possibly influencing the biotransformation of AHA is the surface charge of the biofilm and AHA molecules. Zhang and Bai (2003) reported a pH_{pzc} of 1.6 for AHA, such that AHA surface charge is negative at pH > 1.6. The negative surface charge is due to deprotonation of carboxylic and phenolic groups. Accordingly, a possible electrostatic repulsion between AHA and negatively-charged biofilm surface may adversely affect the adsorption/transport of AHA into biofilm matrix.

At a velocity of 34 cm/h, both pyrrole and leucine with more than 97% DON removal efficiency and 55% average ammonification had the best performance of simultaneous adsorption and biotransformation among the examined organic nitrogenous compounds. The pyrrole average ammonification of 55 ± 4% was surprisingly higher than percentages for readily biodegradable urea. At 61 cm/h, ammonification did not exceed 26% and DON removal efficiency < 40% for the remaining examined compounds. Based on the results and discussion above, effective ammonification in bioretention systems at 22 ± 2°C requires stormwater superficial velocities less than 34 cm/h (EBCT > 27 min).

Based on the results discussed above, integration of adsorption and biotransformation appears to have beneficial effects on stormwater DON removal: enhancement of the ammonification rate, ammonification of the bio-recalcitrant organic nitrogenous compounds, e.g. pyrrole, and bioregeneration of the adsorbent (coal AC). While both urea and leucine are bioavailable compounds, adsorbability on coal AC is the major difference between them. According to Table 4-1, coal AC adsorption capacities of urea and leucine are < 0.01 and 0.10 mg/g at C_e = 1 mg N/L, respectively. Average ammonification for urea was only 13 ± 2%, lower than the 26 ±

2% for leucine at 61 cm/h, indicating the importance of adsorption on DON ammonification rate.

Comparing pyrrole and AHA indicates that adsorption may assist in the biodegradation of bio-refractory organic compounds. While average ammonification for AHA was 9 ± 0%, it was 55 ± 4% for pyrrole at velocity of 34 cm/h. Pyrrole, unlike AHA, is highly adsorbable on coal AC (Table 4-1). Addition of activated carbon to an activated sludge system was found to improve the removal of bio-recalcitrant compounds in other studies (Scaramelli and DiGiano, 1973; Nayar and Sylvester, 1979; Çeçen, 1994; Lim and Er, 2000; Lee and Lim, 2005).

Another apparent benefit from integration of adsorption and biodegradation can be bioregeneration. Coal AC sites adsorbing DON are likely to be regenerated after biotransformation of adsorbed DON to ammonium and release of the generated ammonium into the effluent. For example, the leucine column showed signs of bioregeneration (Figure 4-1). At the end of the 34 cm/h phase, the average DON removal efficiency of leucine was almost 100% obtained at an applied depth of 428 m, while the exhaustion depth for adsorption of leucine on coal AC was estimated as only 8.8 m for the same column (based on the adsorption capacity of 0.10 mg N/g presented in Table 4-1). Bioregeneration of activated carbon saturated by organic compounds has been reported by DeWalle and Chian (1977); Chudyk and Snoeyink (1984); de Jonge et al. (1996); and Lee and Lim (2005).

Effect of temperature on DON biotransformation

Figure 4-2 shows effluent cumulative ammonium changes as a function of applied depth for leucine ammonification in the coal AC-packed column at two temperatures

of 22 ± 2 (room temperature) and 4°C. Low temperature has a dramatic effect on bacterial activities driving biochemical systems (Abrajano et al., 2007; Speight, 2017). Thus, if ammonification becomes a principal tool for stormwater DON removal, bioretention performance may be compromised during cold weather. Despite the general fact that bacterial activities decrease as temperature drops, leucine ammonification seems not affected by temperature decreasing to 4°C at a velocity of 34 cm/h. At 61 cm/h, however, temperature of 22 ± 2°C showed better performance compared to 4°C such that effluent cumulative ammonium mass production decreased by 58% at 4°C (applied depth of 796 m).

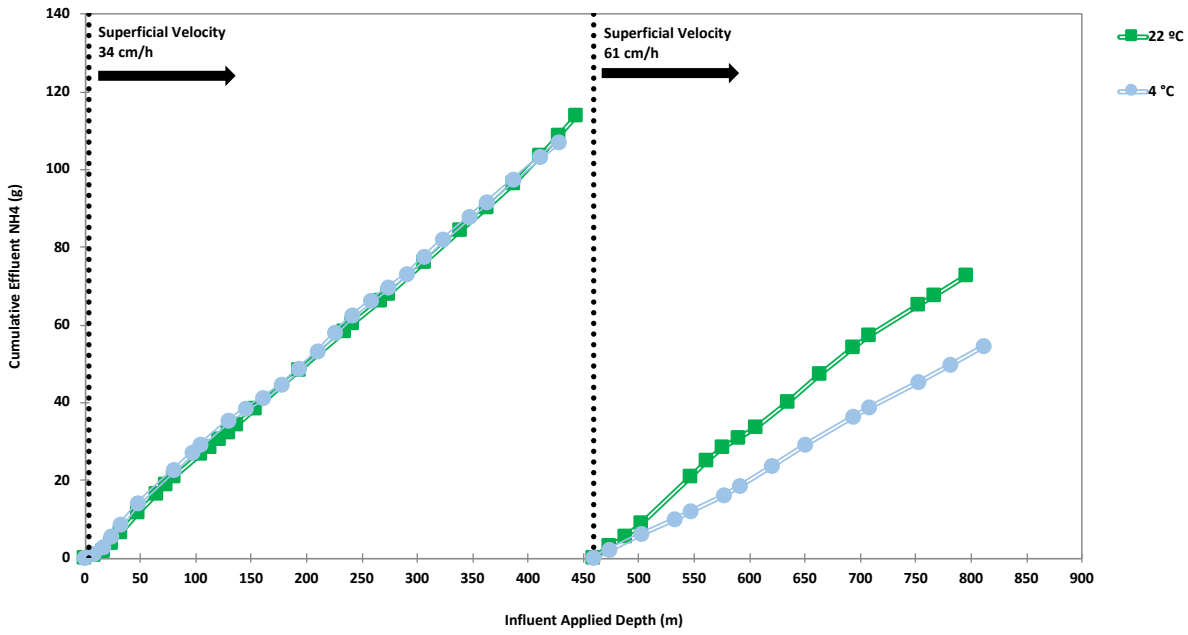


Figure 4-2. Biotransformation of leucine to ammonium on coal AC at two superficial velocities (34 and 61 cm/h) and two temperatures (22 ± 2 and 4°C). Bed height = 15 cm; Bed mass = 43 g; Influent concentration = 1 ± 0.1 mg N/L; Background electrolyte = 0.01M NaCl.

Ammonification principally occurs between 15 and 60 ºC and its rate becomes faster as temperature gets closer to 60 ºC (Panganiban, 1925) while the optimum

temperature lies between 40 and 60°C (Kadlec and Wallace, 2008; Vymazal, 2007; Vymazal et al., 2006; Saeed and Sun, 2012). Ammonification is less sensitive to temperature compared to nitrification/denitrification such that it takes place more readily than nitrification at soil temperatures < 10 ºC (Emmer and Tietema, 1990). Schütt et. al. (2014) found that gross ammonification almost stopped at -4 ºC and 88-96% increase was observed as soil temperatures increased to 8 ºC. Accordingly, the results from the current research and previous studies suggest ammonification as a possible reliable mechanism for stormwater DON removal at low temperatures as long as it is not lower than 4°C.

The velocity, however, may boost temperature effects on ammonification, as seen for 61 cm/h. As the velocity increases, the contact time between leucine molecules and the adsorption media surface decreases and compromises adsorption of leucine; as a possible result, the retention time of leucine in the adsorption/biotransformation column decreases. Such a condition might expose the effect of reduced ammonification rate at the low temperature of 4°C after the increase of velocity to 61 cm/h. In conclusion, it is suggested that both temperature and velocity need to be considered together for an effective stormwater DON ammonification, such that it is expected that at lower temperatures, longer contact times are required.

Effect of bed material type on DON biotransformation

Figure 4-3 presents effluent cumulative ammonium as a function of applied depth for leucine ammonification on three different bed materials: coal AC, quartz sand, and charcoal. Because quartz sand and charcoal are less expensive than coal AC, a reasonable ammonification performance makes less-expensive materials more

desirable compared to coal AC. However, at applied depth up to 129 m, coal AC had better performance such that the effluent cumulative ammonium for coal AC is 2.5 and 8.3 times of that for charcoal and quartz sand, respectively.

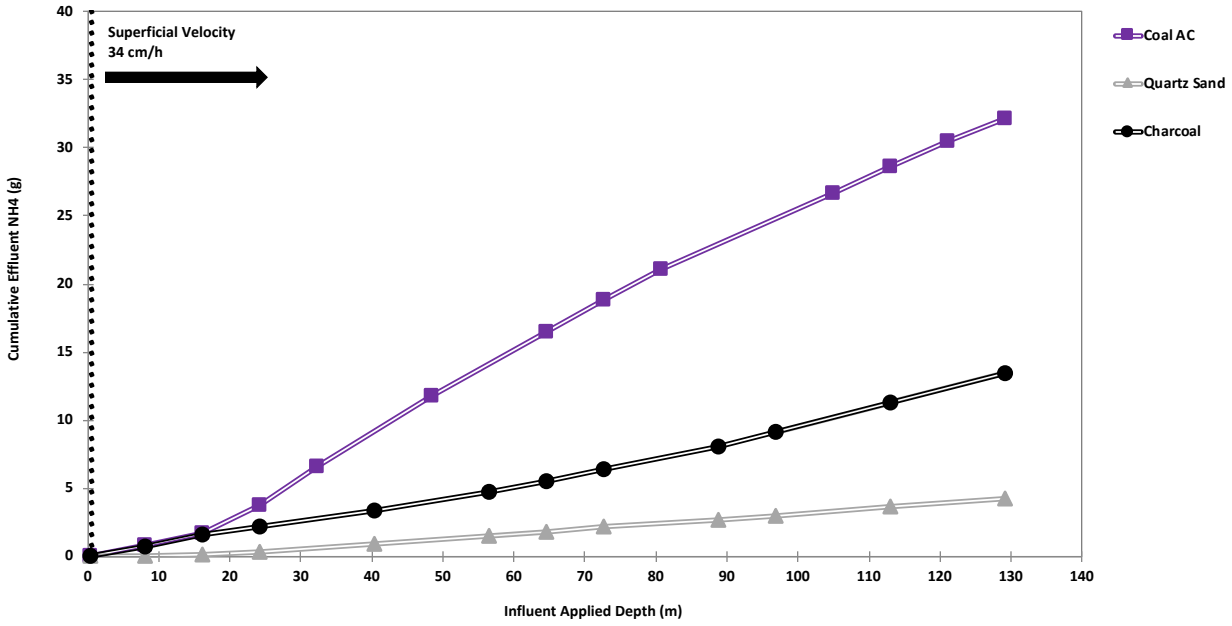
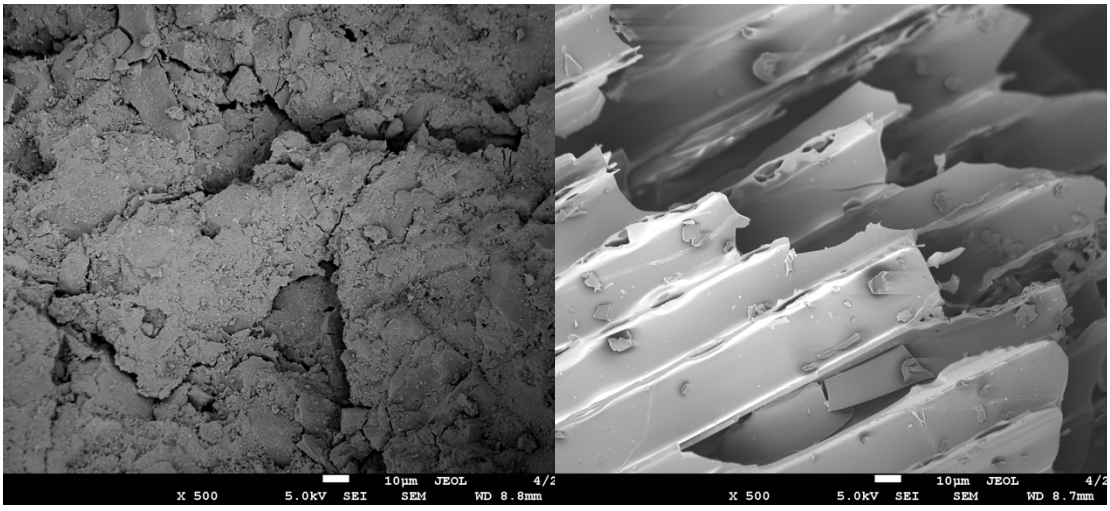


Figure 4-3. Biotransformation of leucine to ammonium on three bed materials: coal AC (43 g), quartz sand (61 g), and charcoal (23 g) at superficial velocity = 34 cm/h. Bed height = 15 cm; Influent concentration = 1 ± 0.1 mg N/L; Background electrolyte = 0.01M NaCl; Temperature = 22 ± 2°C.

As presented in Table 4-2, coal AC has the largest specific surface area (798 m^2/g) and the largest pore volume (0.198 mL/g) among the examined materials. Unlike quartz sand with a porosity of 37 ± 1%, both charcoal and coal AC are very porous materials with porosities of 57 ± 2% and 59 ± 1%, respectively. The porosity of charcoal and coal AC is also obvious in their scanning electron microscopy images (Figure 4-4). Porous materials like granular activated carbon, with various micro- and macro-pores, provide much larger specific surface area compared to quartz sand possessing non-porous surface (Suárez-Ruiz and Crelling, 2008; Yapsakli and Çeçen, 2010; Singh,

2015). Quartz sand has smooth surfaces, but the granular activated carbon surface is rough with widely distributed crevasses/ridges enhancing microbial attachment (Hattori, 1988). The amorphous structure of granular activated carbon can also protect attached bacteria from shear forces preventing biofilm formation (Urfer et al., 1997; Liu et al., 2001). All of these benefits might contribute to desirable performance of coal AC for leucine ammonification.

As noted, the initial phase in the biofilm development is the adsorption and coating of organic compounds on bed material (Trulear and Characklis, 1982). This initial organic layer is a prerequisite for the later microbial attachment (Baier, 1973; Fletcher, 1980). Mohtadi et al. (2017) could not detect any signs of leucine adsorption on charcoal. Despite both charcoal and coal AC having large and similar specific surface area and pore volume, lack of leucine adsorption on charcoal possibly curbed formation of an initial organic layer providing less ammonification compared to coal AC.



(a) (b)

Figure 4-4. Scanning electron microscopy images of granules of (a) coal AC and (b) charcoal – zoom 500x

Effect of bed height (contact time) on DON biotransformation

Figure 4-5 presents effluent cumulative ammonium as a function of applied depth for leucine ammonification on three coal AC-packed columns with different bed heights of 15, 30 and 50 cm. At a velocity of 34 cm/h, effluent cumulative ammonium increased by similar slopes for all three columns up to applied depth of 145 m; beyond this point, both 30- and 50-cm columns showed better performance than 15-cm. By increasing the velocity to 61 cm, effluent cumulative ammonium increased faster in the 50-cm column than the 15- and 30-cm columns. Both 15- and 30-cm columns shared similar slope. The 30-cm column clogged at the end of the 34 cm/h phase and the column was repacked with new coal AC material for the 61 cm/h velocity phase. Compromised performance by the 30-cm column at this velocity should be related to the lack of developed biofilm in the newly repacked column.

Carlson (1996) found that organic compound removal is sensitive to EBCT, and not superficial velocity. At a fixed velocity, contact time changes by changing the bed heights. LeChevallier et al. (1992) reported that biological removal of total organic carbon in a biofilter increased to 29, 33, 42, and 51% at 5, 10, 15, and 20 min EBCT at fixed velocity, indicating that biological removal non-linearly changes with contact time. In the current study, at 34 cm /h, the effluent cumulative ammonium increased by 31% as EBCT increased from 27 min (15-cm column) to 54 min (30-cm column). No noticeable difference, however, could be determined as EBCT increased from 54 min (30-cm column) to 89 min (50-cm column). Other studies have shown that biomass density changes throughout the column height, decreasing from influent point to effluent point (Urfer et al., 1997; Velten et al., 2011). Accordingly, increasing the bed

height (contact time) beyond a specific height (time) does not necessarily improve ammonification efficiency, as seen for 30- and 50-cm columns.

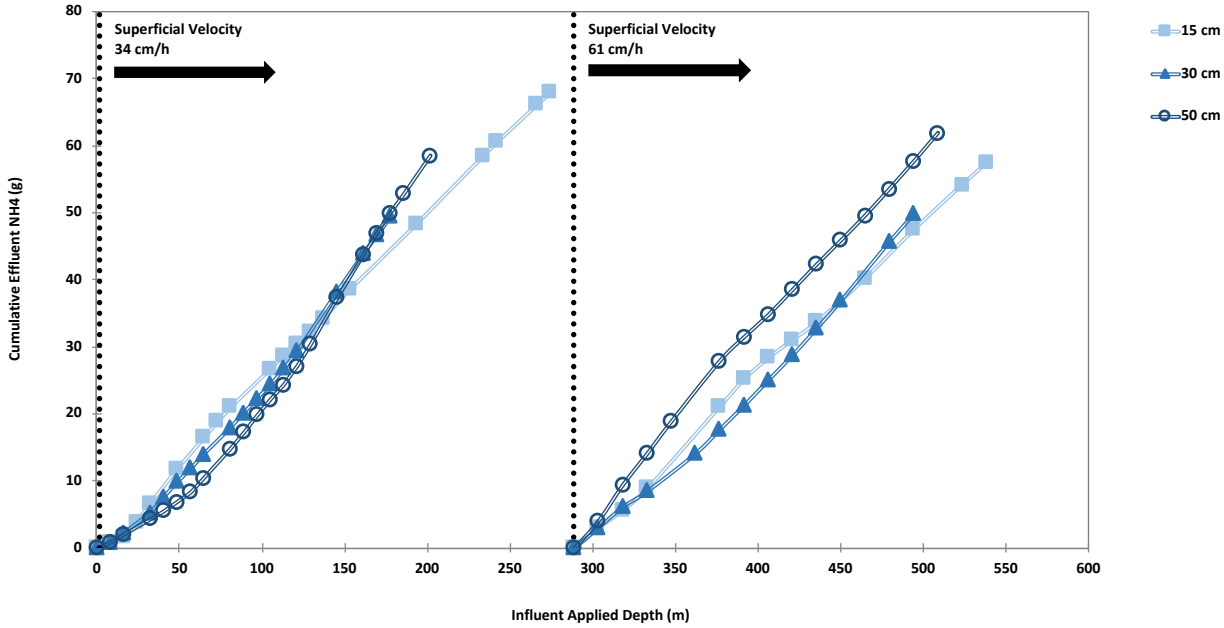


Figure 4-5. Biotransformation of leucine to ammonium on coal AC at two superficial velocities (34 and 61 cm/h) with three bed heights: 15-cm (43 g), 30-cm (89 g), and 50-cm (145 g); Bed height = 15 cm; Influent concentration = 1 ± 0.1 mg N/L; Background electrolyte = 0.01M NaCl; Temperature = 22 ± 2°C.

Effect of wetting/draining regime on DON biotransformation

Figure 4-6 shows changes of effluent TN, DON, ammonium, and nitrate concentration dependencies on applied depth for biotransformation of leucine on coal AC with wetting/draining regimes at two velocities, 34 and 61 cm/h. The wetting periods were 24 hours while the draining periods were intermittently 2 and 3 days. Samples were collected at the beginning and end of each wetting period.

Under intermittent wetting/draining conditions, the effluent DON was less than 0.1 mg N/L after the applied depth of 48 m, indicating that DON was successfully removed through simultaneous adsorption/ammonification. The effluent TN was mainly

composed of ammonium and ammonium concentration peaked after each draining period and even reached to more than 15 mg N/L, subsequently it dropped to less than 0.91 mg N/L after each wetting period. As the experiment progressed greater ammonification was noticed, probably due to more influent DON and faster ammonium washout at velocity of 61 cm/h. Nitrate was detected in some samples (concentrations less than 0.19 mg N/L) and nitrite was less than the detection limit of 0.01 mg N/L. However, other studies reported that nitrification and denitrification were enhanced during drying periods more than wetting periods (Cho et al., 2009; Subramaniam et al., 2016).

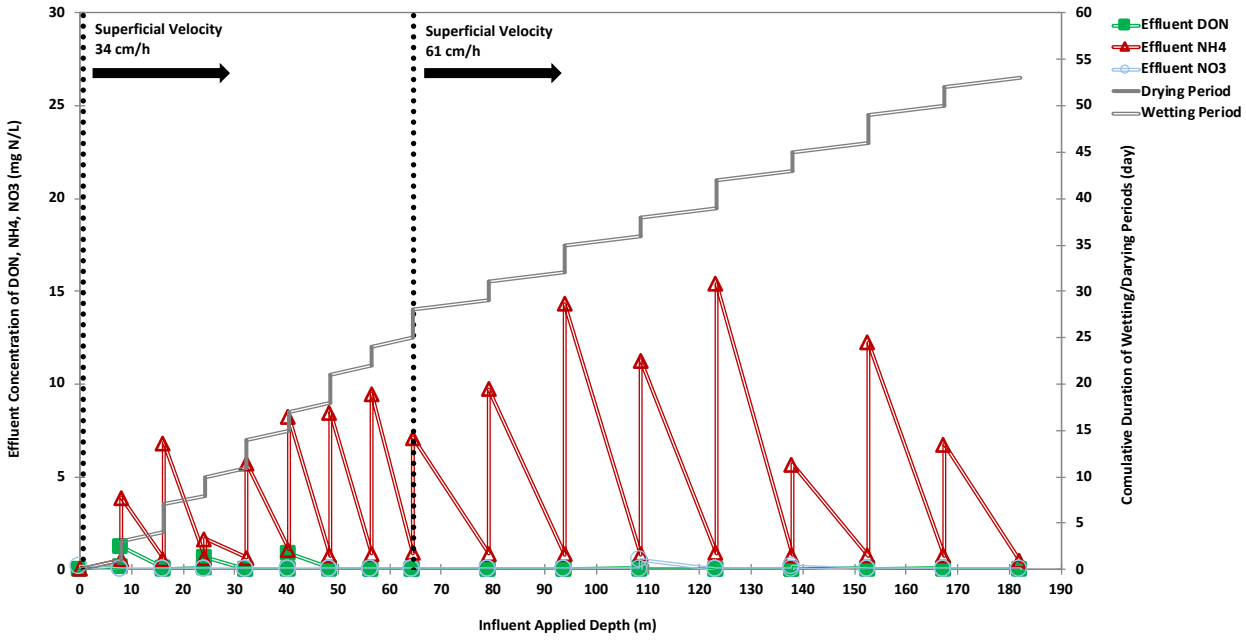


Figure 4-6. Biotransformation of leucine on coal AC at two superficial velocities (34 and 61 cm/h) in intermittent wetting/draining conditions; Bed height = 15 cm; Bed mass = 43 g; Influent concentration = 1 ± 0.1 mg N/L; Background electrolyte = 0.01M NaCl; Temperature = 22 ± 2°C.

Generally in bioretention systems, biological removal of organic compunds mainly occurs during drying periods while adsorption mainly takes place during wetting

periods (LeFevre et al., 2015; Subramaniam et al., 2016). In brief, draining periods successfully promoted ammonification and coal AC bioregeneration in the current study. For an actual bioretention system, by delaying its exhaustion, these results suggest greater chance of stormwater DON biological removal and less need to replace coal AC.

Recommendations for bioretention design enhancing DON biotransformation

Because the main goal of this study was to biologically remove stormwater DON through ammonification, media exhaustion (in terms of effluent TN) was not a concern. Accordingly, discussion on maximum influent applied depth or rainfall depth is not appropriate. The important element is the degree of ammonification and biotransformation of DON to ammonium is more desirable. According to the results from the current study:

- Although continuous dosing experiments indicated that the superficial velocity should be kept less than 34 cm/h, the intermittent wetting/draining experiment showed that ammonification would not be impacted at 61 cm/h for leucine. Additionally, temperature as low as 4°C impacted the ammonification at 61 cm/h, but not at 34 cm/h. Thus, the maximum superficial velocity should be kept at 34 cm/h or less.
- The ammonification layer should be composed of coal AC and its maximum thickness should be 30 cm. Larger thickness should not improve ammonification.

The DON ammonification/adsorption layer in bioretention can be placed right after the first top mixed-layer of sand and plant soil (rhizosphere zone). This is because the

generated ammonium can be removed through adsorption and nitrification/denitrification processes in bioretention lower layers.

Conclusions

This biotransformation study on five organic nitrogenous compounds (urea, leucine, NAG, pyrrole, and humic acid) with different adsorbability on coal AC and bioavailability showed that adsorption is a more important controlling factor for ammonification than is bioavailability. Bio-recalcitrant pyrrole and biodegradable leucine demonstrated the best performance with respect to DON removal efficiency (98 ± 2% and 97 ± 3%, respectively) and ammonification (55 ± 4% and 55 ± 1%, respectively) among the examined compounds. These two compounds are medium-to-highly adsorbable on coal AC. On the other hand, both bio-recalcitrant AHA and biodegradable urea are low to medium adsorbable on coal AC and both had very low ammonification, 9 ± 0% % and 2 ± 2%, respectively. Although the NAG column showed promising results at first, it failed due to clogging.

Comparing simultaneous adsorption and biotransformation of these five compounds also showed three apparent benefits: enhancement of the ammonification rate, ammonification of the bio-recalcitrant organic nitrogenous compounds, e.g. pyrrole, and bioregeneration of the adsorbent (coal AC). Also, effects of three factors, temperature, bed media type, and bed media height were tested. Low temperature (4°C) did not impact ammonification of leucine at the velocity of 34 cm/h, but negatively affected it at 61 cm/h. Three bed media, coal AC, charcoal, and quartz sand were examined, and it was found that coal AC had the best performance for simultaneous adsorption and biotransformation of organic nitrogenous compounds. Although coal

AC and charcoal are both porous materials, apparently the adsorption properties of coal AC made it a better material for biofilm formation and DON ammonification. By testing three bed media heights (15, 30, and 50 cm), it was observed that bed media height > 30 cm would not increase ammonification.

Under intermittent wetting/draining conditions, the effluent DON was less than 0.1 mg N/L after an applied depth of 48 m, indicating that DON was successfully removed through simultaneous adsorption/ammonification. The effluent TN was mainly composed of ammonium and ammonium washout sharply increased after each draining period. Unlike continuous dosing, DON ammonification was not negatively affected by increasing the superficial velocity from 34 to 61 cm/h. The generated ammonium can be managed through nitrification/denitrification and plant up-take (Cho et al., 2009; LeFevre et al., 2015) in SCMs, and/or adsorption on proper materials such as zeolite and aluminosilicate (Khorsha and Davis, 2017b, 2017a).

Chapter 5: Bioretention Design Recommendations for DON Removal

Based on the results obtained from the current study and previous studies, some recommendations can be made for bioretention design regarding removal of stormwater DON. A layer of coal AC + quartz sand (70:30 by mass) or single coal AC is recommended; the amount of coal AC determines the lifetime of the bioretention media. The height of the DON removal layer is recommended to be 30 cm or less because both column adsorption and biotransformation studies showed that media bed height greater than 30 cm did not appreciably improve DON adsorption or ammonification performance. The recommended depth for conventional bioretention media is about 1.2 m (Davis et al., 2009), thus a 30-cm layer allows enough space for inclusion of other possible media materials to remove other stormwater pollutants.

Typical bioretention infiltration rates vary from 1.3 to 5.1 cm/h (Davis et al., 2009), which can be adjusted by media porosity and water head. The results from the column adsorption kinetics suggest organic nitrogenous compounds similar to pyrrole are minimally affected by increased flowrate (decreased contact time between organic nitrogenous compound and bioretention media), such that the design infiltration rate could be increased up to 500 cm/h. However, the results for other compounds (except pyrrole) suggests the infiltration rate should be as low as 7 cm/h. Continuous dosing biotransformation experiment indicated that the superficial velocity should be kept less than 34 cm/h, but the intermittent wetting/draining experiment showed that ammonification would not be impacted at 61 cm/h. Another point is that temperature

as low as 4°C impacted the ammonification percentage at 61 cm/h, but not at 34 cm/h. By considering results from both adsorption and biotransformation studies, the maximum infiltration rate is recommended to be approximately 34 cm/h or less. This range is comparable to comparable to 20-40 cm/h used in slow sand filters (Fox et al., 1994). If it is assumed that no ammonification occurs, actual stormwater DON = 1.0 mg N/L, and typical annual rainfall depth for the Washington DC Metropolitan Area = 100 cm, a 30-cm layer of coal AC + quartz sand (70:30 by mass) with superficial velocity 61 cm/h can last for 88 months before the exhaustion of bioretention media.

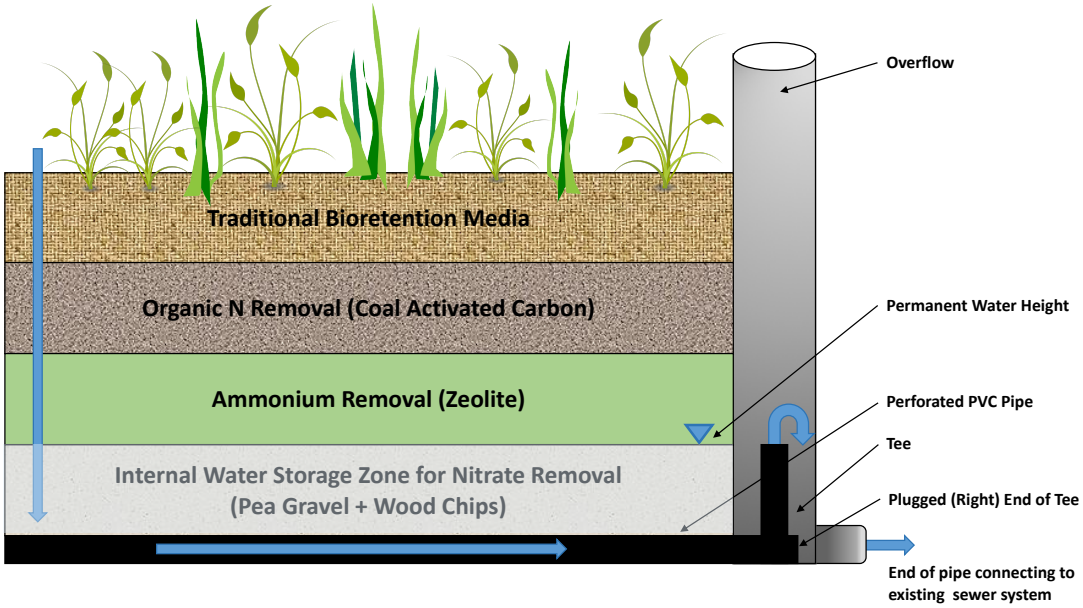


Figure 5-1. Schematic diagram of a bioretention cell with emphasis on nitrogen removal

Regarding bioretention layering with emphasis on DON removal, four major layers are considered. The top layer is a mixed layer of traditional bioretention media located in the rhizosphere to promote vegetation, which may enhance removal of stormwater nitrate (Li et al., 2019; Muerdter et al., 2019). Also, a study by Näsholm et al. (2009)

confirms the ability of plants to directly acquire amino acids from soil. A second layer consisting of coal AC (or mixed with sand quartz as discussed above) is suggested to first adsorb DON and subsequently encourage mineralization of the captured DON, although highly soluble compounds such as urea may not be effectively adsorbed. If deep-rooted plants are placed in bioretention, the second layer may also be part of the rhizosphere. The ammonium generated in the DON layer may be either taken up by the deep-rooted plants or washed out to lower bioretention layers where it may be removed through adsorption and nitrification/denitrification processes.

To address ammonium wash-out from upper layers, a third layer of ammonium-adsorbing material is suggested to adsorb ammonium and enhance its biotransformation to nitrate. Ammonium can be adsorbed by some materials, including clays, zeolites and silicates through cation-exchange process (Rožić et al., 2000; Hedström, 2001; Khorsha and Davis, 2017b, 2017a). Ammonium was also shown to be removed through adsorption on sandy coarse/fine soil layer during stormwater dosing followed by nitrification during subsequent dry periods (Cho et al., 2009). As a recommendation, layers for removal of DON and ammonium may be merged/mixed, such that the generated ammonium can be held in the same layer.

Nitrate/nitrite, which is not captured and is washed out from the upper layers, can be removed through an anoxic internal water storage (IWS) as the bottom layer. This fourth layer, made of sand/gravel and an organic carbon source, is designed to stay saturated between storm events and develop anoxic conditions promoting denitrification (Kim et al., 2003; Hsieh et al., 2007; Ergas et al., 2010; Peterson et al., 2015; Igielski et al., 2019). Inoculation with sand previously used for slow sand filters

can improve functioning of new slow sand filters (Chan et al., 2018); the idea of inoculation with microbial cultures from water treatment plants can be considered for use in bioretention systems. **Error! Reference source not found.** summarizes the recommendations given above and the order of bioretention layers considered for removal of DON, ammonium and nitrate/nitrite.

It must be noted that the recommendations above are based on the findings from the current study using the synthetic stormwater containing single organic nitrogenous compounds. The presence of other organic and inorganic compounds may affect the removal of the studied organic nitrogenous compounds. It has been found that the presence of natural organic matter can reduce the adsorption efficiency of activated carbon for organic micropollutants because of competing effects, site covering effects and pore blocking effects (L. Ding, 2010). The binary adsorption study by Terdkiatburana et al., (2008) has shown that complexation of copper ions and humic acid could increase adsorption of copper ions but competitive adsorption between lead ions and humic acid could lead to decrease in adsorption of both lead ions and humic acid on activated carbon. Chen et al. (2007) also found that co-adsorption of copper ions decreases adsorption of both examined polar and nonpolar compounds. On other hand, the data collected showed that the adsorption capacity of phenol was not affected by the presence of copper ions in the system (Jiang et al., 1992).

Another possible concern is accumulation of calcium carbonate on activated carbon surfaces. Lee et al. (2003) have found that both adsorption and biotransformation of the examined organic compounds on granular activated carbon could be compromised because of accumulation of calcium carbonate. Accordingly, possible negative/positive

effects of the presence of other organic and inorganic compounds on actual stormwater DON removal should be examined before designing full-scale bioretention systems for actual use in stormwater DON removal.

Chapter 6: Conclusions and Recommendations for Future Research

The batch adsorption phase evaluated the adsorption of eight organic nitrogenous compounds with different chemical properties on several adsorbents (including coal activated carbon, coconut-shell activated carbon, charcoal, peat, chitosan, WTR, calcite, montmorillonite, zeolite and quartz sand). For most of the examined adsorbates and adsorbents, either the adsorption capacity was negligible, or nitrogen leached from the adsorbents.

The results revealed that only two of the tested organic nitrogenous compounds (pyrrole and NAG) were strongly adsorbed by both coal and coconut-shell ACs, while coal AC was preferred due to phosphorus release by coconut-shell AC. The adsorption capacity of coal AC (q_e) for pyrrole and NAG were 0.4 mg N/g (at C_e = 0.02 mg N/L) and 0.71 mg N/g (at C_e = 1 mg N/L), respectively. Other organic nitrogenous compounds including leucine, lysine, glutamic acid, serine, and AHA were partially adsorbed on coal AC (q_e < 0.1 mg N/L at C_e = 1 mg N/L) while adsorption capacity for urea was negligible (q_e < 0.01 mg N/g). Moreover, the removal efficiency of actual stormwater DON (at initial DON concentration of 0.63 mg N/L) by both ACs was similar to removal efficiencies of pyrrole and NAG (at initial DON concentration of 0.49 ± 0.08 mg N/L). The adsorption kinetics study suggests 1-2 hour contact time between DON and coal AC to reach 80-90% of ultimate adsorption capacity for highly adsorbable compounds such as pyrrole and NAG, and about 60% or less for other tested organic nitrogenous compounds at initial DON concentration of 1 mg N/L. Based on

these results, it is concluded that a part of stormwater DON can be appreciably removed through adsorption processes, similar to adsorption of pyrrole and NAG on coal AC.

In the continuous column adsorption phase, the adsorption of synthetic stormwater DON was evaluated under more realistic conditions (continuous flowrate). The eight different organic nitrogenous compounds used in the batch adsorption study, were also examined for continuous column adsorption on coal AC. Pyrrole was the only compound which was appreciably adsorbed by the media mixture of coal AC + quartz sand. Unlike the batch adsorption results, the column adsorption of NAG was compromised, possibly due to formation of a thin clear film, a so-called hydrogel, on the media mixture. The breakthrough and exhaustion depths for pyrrole were 88 and 499 m (equivalent to 4.4 and 25.0 m simulated rainfall depth), respectively, at a fixed superficial velocity of 61 cm/h and fixed influent DON concentration of 1 mg N/L. The breakthrough depth for other organic nitrogenous compounds was less than 15 m and their exhaustion depths lied between 44 and 191 m.

More tests on the column adsorption of pyrrole using a media mixture of coal AC + quartz revealed that pyrrole adsorption was minimally affected by flowrate increase, such that pyrrole removal efficiency stayed > 91% for all the tested superficial velocities (7 to 489 cm/h). Also, it was found that media bed height greater than 30 cm did not appreciably improve pyrrole exhaustion depth. The exhaustion depths for 15-, 30- and 50-cm bed heights were 499, 1042, and 1291 m (equivalent to 25.0, 52.1, and 64.6 m simulated rainfall depth), respectively. According to these results, adsorption processes can be relied on for removing any part of actual stormwater DON being adsorbed similar to pyrrole. However, to remove weakly-adsorbable stormwater DON,

adsorption is possibly inadequate and other treatment measures should be considered. In the column study, unintended DON ammonification occurred despite prevention measures, which suggests an alternative approach for removing that fraction of stormwater DON not effectively adsorbed by coal AC.

The biotransformation phase studied five organic nitrogenous compounds (urea, leucine, NAG, pyrrole, and humic acid) with different bioavailability and adsorbability on coal AC. Bio-recalcitrant pyrrole and biodegradable leucine demonstrated the best performance with respect to DON removal efficiency (98 ± 2% and 97 ± 3%, respectively) and ammonification percentage (55 ± 4% and 55 ± 1%, respectively) among the examined compounds. These two compounds are medium to highly adsorbable on coal AC. On the other hand, both bio-recalcitrant AHA and biodegradable urea are low to medium adsorbable on coal AC and both had very low ammonification percentage, 9 ± 0% % and 2 ± 2%, respectively. Although the NAG column showed promising results at first, it failed due to clogging.

Comparing simultaneous adsorption and biotransformation of these five compounds also showed three apparent benefits: enhancement of ammonification rate, ammonification of bio-recalcitrant organic nitrogen compounds, and adsorbent (coal AC) bioregeneration. Also, effects of three factors: temperature, bed media type, and bed media height on ammonification were tested. Low temperature (4°C) did not impact ammonification of leucine at the velocity of 34 cm/h, but negatively affected it at the velocity of 61 cm/h; accordingly, ammonifiction might be considered as a possible reliable mechanism for stormwater DON removal at low temperatures as long as it is not lower than 4°C and the velocity is lower than 34 cm/h. Three different bed

media: coal AC, charcoal, and quartz sand were examined; it was found that coal AC had the best performance for simultaneous adsorption and biotransformation of organic nitrogenous compounds. Although coal AC and charcoal are both porous materials, apparently the adsorption properties of coal AC turned it to a better material for biofilm formation and DON ammonification. By testing three bed media heights (15, 30, and 50 cm), it was observed that bed media height > 30 cm did not increase ammonification percentage, which was possibly due to non-uniform biomass distribution throughout the column depth.

Under intermittent wetting/draining conditions, the effluent DON was less than 0.1 mg N/L after the applied depth of 48 m, indicating that DON was successfully removed through simultaneous adsorption/ammonification. The effluent TN was mainly composed of ammonium and its concentration sharply increased after each draining period. Unlike continuous dosing, DON ammonification was not negatively affected by increasing the superficial velocity from 34 to 61 cm/h. The generated ammonium, however, is required to be addressed by appropriate stormwater treatment methods. Further studies, especially on actual stormwater, is required to make a more reliable conclusion; however, the simultaneous adsorption/ammonification appears to be an effective method for removal of a part of stormwater DON.

Unlike inorganic nitrogen, many different types of organic nitrogen with different chemical/physical properties exist in nature, which makes it hard to recommend a single strategy for stormwater DON removal. Based on the results from the current study, some DON types were strongly adsorbed by adsorbents, e.g., adsorption of pyrrole on coal AC; some were more bioavailable, e.g., ammonification of leucine; and

some were barely adsorbable and bioavailable, e.g., AHA on coal AC. Accordingly, both adsorption and biotransformation should be considered to enhance stormwater DON removal as much as possible.

For further research, some recommendations are available. First, adsorption of stormwater DON may be enhanced through modification of the adsorbent surface or application of other adsorbents. By modification, functional groups and/or the charge of the adsorbent surface may change in favor of adsorption of a specific organic nitrogenous compound. For instance, glutamic acid may be in the form of a negatively-charged ion in stormwater at neutral pH, 6.5-7.2 (Minton, 2005); if a surface modification by changing pH_{zpc} develops a positive charge on the adsorbent surface at the same pH, the chance for adsorption of glutamic acid may increase. Also, a new adsorbent may be found with a surface charge that stays positive at the same pH.

Regarding application of biotransformation in stormwater DON removal, recommendations can be made for further research: seeding of bioretention media for biofilm development and use of actual stormwater instead of synthetic. Seeding might improve DON biotransformation by enhancing biofilm diversity. Running laboratory-based experiments of DON biotransformation by using actual stormwater would return more practical results to use in designing of bioretention systems. For instance, possible negative/positive effects of the presence of other organic and inorganic compounds on actual stormwater DON removal can be observed. Finally, studying an actual bioretention with separate layers designed to remove PON, DON, ammonium and nitrite/nitrate from stormwater, would be a reasonable recommendation for further research. This is because trapped PON can be converted to DON, then to simpler forms

including ammonium and nitrite/nitrate; accordingly, all these nitrogen forms should be addressed all together for effective stormwater nitrogen removal.

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